XXVII. — THE CONSTITUENTS OF PENNSYLVANIA, OHIO, AND CANADIAN PETROLEUM BETWEEN 150° AND 220°.

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The conflicting statements published long ago, and still uncorrected, concerning the composition of the portions of Pennsylvania petroleum distilling above 150°, the absence of any information relating to the constituents of Ohio and Canadian petroleum, and the erroneous assumptions as to the composition of American petroleum based on the results of Markownikoff and his assistants in the Russian oil, taken together, render a study of these portions of American petroleum of extreme interest. One cannot fail to be impressed with the marked differences of opinion that have prevailed as to the composition of the portions of American petroleum with higher boiling points. Some authorities, influenced by the profound investigations of the Russian chemists on the Caucasus oil, have believed that the constituents of American oil above 150° are naphtenes, with a reservation as to whether the series C_nH_{2n} announced by Warren should be accepted as naphtenes. Others, depending on the results of Pelouze and Cahours, which form the basis of the statements in chemical literature concerning the constituents of these petroleums, have held that the series C_nH_{2n+2} does not find its last representative in nonane, boiling point 151°. Similar differences of opinion have been expressed by practical oil men, those who have witnessed the development of the petroleum industry from the beginning, concerning the composition of these oils. Some believe that Canadian and Ohio oils are essentially and fundamentally different from the Pennsyvania oil. Others hold that the chief constituents are identical, and that differences observed in refining are due to variations in the proportions of the principal constituents, and to the presence in some oils of small amounts of other bodies that are not found in all. I must admit that my earlier impressions on this subject have not been verified in the light of the results which will be presented.

This work was undertaken with the expectation that Pennsylvania oil would prove to consist in its higher portions of a series C_nH_{2n}, and it is only after a great amount of laborious study, and a vast accumulation of analytical data, presenting unquestionable evidence that, for the hydrocarbons distilling within these limits of temperature, except those collecting at 196° and 216° from Canadian petroleum, this series must be discarded, that I accept this conclusion. Concerning the composition of Ohio and Canadian petroleum, in the beginning of this work, I had no preconceived ideas.

The separation of constituents with higher boiling points presents greater difficulties than those in the portions distilling below 150°. In the lower portions there is no danger of decompositions during distillation, both on account of greater stability of the hydrocarbons and because the unstable bodies, such as the nitrogen, oxygen, and sulphur compounds, as well as the more complex hydrocarbons, distil for the most part at higher temperatures. Then distillation in air has little if any effect on the lower constituents, while the portions distilling at higher temperatures cannot be volatilized in the presence of air without more or less decomposition. As has been shown, distillation *in vacuo* prevents changes due to inherent instability and it excludes air, but it increases very much the labor of the separations. It has been found to be especially serviceable in separating the hydrocarbons under consideration, since these bodies are contained for the most part in portions of the first distillate boiling above the limits of cracking, and are consequently contaminated by the products of decomposition when distilled in air, and the decomposition products are difficult to remove. Evidently any experiments on a laboratory scale may fail to reveal the presence of bodies that are present in proportionately minute quantities. It would be interesting, and from a commercial point of view doubtless profitable, to establish a more extended investigation involving the manipulation of at least a hundred barrels of crude oil, continuing the fractional separations of all portions until the individual hydrocarbons were as perfectly isolated as is done with smaller quantities in the laboratory. Such an investigation could only be undertaken at large expense, and a long time would be required to reach desirable results.

In undertaking this subject, the course to be followed was plain. There is but one method for the separation of these hydrocarbons, and it yields satisfactory results only after long and tedious application. Concerning the question as to whether fractional distillation can be relied on for the separation of hydrocarbons with boiling points not far removed,

it can, I think, be stated with confidence that distillations many times repeated under constant conditions may be expected to yield products whose composition can be determined, after suitable purification, as accurately as the methods of analysis will permit. But hydrocarbons separated from petroleum in this manner, before purification, may be contaminated by other bodies whose boiling points are nearly the same. As an illustration, to ascertain whether Ohio petroleum contains a hydrocarbon boiling at 162°, a course of fractional separations under 730 mm. was repeated fifty times, forty-five times within one degree. One portion after treatment with fuming sulphuric acid had its specific gravity changed from 0.7717 to 0.7535, but it still distilled within the same limits. Another portion of the same distillate, after treatment with common concentrated sulphuric acid, gave a product with the same specific gravity and the same boiling point as the oil before treatment. The crude distillate contained a certain amount of mesitylene, boiling point 163°, sufficient, as will appear later, to affect seriously the percentages of carbon and hydrogen. In the main, the hydrocarbons described in this paper as collecting between 160° and 216° have the same boiling points as those described by Warren, except one which collected at 162°. It is peculiar that these bodies have nearly the same boiling points as the naphtenes separated by Markownikoff from the Russian oil. In previous investigations on these hydrocarbons, except those of Warren, evidently the course of distillation was not carried far enough to separate with any degree of purity the individual constituents. In the light of Warren's distillations and those here presented, it is evident that Pelouze and Cahours could not have carried their separations far enough to obtain individual products. Concerning the thoroughness of Warren's separations there can be no question. But the deficiency in his work on the hydrocarbons now under consideration was the result of the limited knowledge then prevailing concerning the general composition of petroleum. The aromatic hydrocarbons, the oxygen compounds, and the nitrogen compounds, were not then recognized, or were merely suspected as constituents of petroleum. In the purification of his distillates, the single method adopted by Warren consisted in boiling with sodium, as shown by the following statement: "I must state, however, once for all, that, unless specially mentioned, no one of the bodies operated upon had received any chemical treatment except that of boiling with sodium." * But that Warren suspected the presence in his distillates of other bodies is indicated by a quotation from

* Proc. Amer. Acad., XXVII. 66.

one of his private papers, already mentioned in another paper: "The samples analyzed may have contained traces of more highly hydrogenized substances, and that it would be worth while to treat with $HOSO_2$, and $HONO_2$, and remove these."* It is evidently an error to consider the hydrocarbons C_nH_{2n+2}, especially the lower members, as unstable toward reagents. It has been our experience, in removing aromatic hydrocarbons from the distillate 160°–216°, that the principal constituents are not affected in the cold by a mixture of nitric and sulphuric acids, nor by fuming sulphuric acid even by warming. After purification, the boiling points do not change in a long course of distillations. No doubt the stability diminishes with a rise in boiling points, but it is sufficient to permit of purification of the members below 216°. All analyses in this paper point to the general composition C_nH_{2n+2}, except for the Canadian hydrocarbons 196° and 216°. If continued distillation or treatment with the means of purification we have adopted produces decomposition, the products should scarcely consist at least entirely of lower members of the same series.

In the comparative examination, the results of which will be described in this paper, two principal objects were kept in view, one of chief importance to determine the series of hydrocarbons which form the main body of American petroleum, and the other naturally following, to ascertain whether the composition of Pennsylvania, Ohio, and Canadian oils as regards their principal constituents is the same.

In undertaking a study of the portions of petroleum within the limits of temperature mentioned above, it was at first determined to prepare all distillates from the crude oils, and this has been done in part in the Ohio and Canadian oils. But when it was found that cracking in refining did not begin in any considerable extent below 225°, and that distillates from the refinery resembled in all respects, at least in their principal constituents, those obtained in vacuum distillation, refinery distillates were more freely employed, especially from Pennsylvania oil. But most of the results on Ohio and Canadian oils were obtained in vacuum distillates, the preparation of which was described in a former paper.† Further assurance against decomposition in the Pennsylvania product was gained by selecting during the "run" in the refinery distillation just that portion of the distillates that corresponds in gravity to the constituents desired. Experience showed that heavier portions of the crude distillate should be selected than those corresponding to the constituents

* Proc. Amer. Acad., XXXI. 31. † Ibid., XXXI. 1.

required, since the boiling points invariably decline many degrees in subsequent distillations.

The refinery distillate employed was taken at 48°–50° Baumé, having a specific gravity 0.7892 at 20°. It was very nearly colorless and gave no odor of decomposition. Forty-five litres of this distillate was fractioned within limits of 10°, 5°, 2°, and for a long time within 1°. It gradually collected in heaps, as described by Warren, but the prolonged distillation was necessary to separate higher and lower constituents from the mixtures between.

Concerning the impression that Pennsylvania petroleum has the same composition within these limits as the Russian oil, which is based in part on the results of Warren suggesting the series C_nH_n, and in part on the erroneous statements of Höfer, that Markownikoff found the same series in Pennsylvania that he had reported in Russian oil, it may be stated once for all that this identity is clearly excluded by the great difference in specific gravity of the corresponding distillates, without reference to the differences in percentage composition. These differences in composition are indicated at the outset by the great differences in specific gravity of crude distillates at 16°, as shown by Markownikoff and Oglobine.*

Baku.		American.
150°–200°	0.786	0.757
200°–250°	0.824	0.788
250°–320°	0.861	0.809

The same differences appear between the individual constituents : † —

Baku Naphtenes.		B.P.	Specific Gravity.
Dekanaphtene	$C_{10}H_{20}$	160°–162°	0.795 (0°)
Endekanaphtene	$C_{11}H_{22}$	180°–185°	0.8119 (0°)
Dodekanaphtene	$C_{12}H_{24}$	196°–197°	0.8055 (14°)

And the series C_nH_{2n} of Warren, purified only by distillation and boiling with sodium : ‡ —

		B.P.	Specific Gravity at 0°.
Rutylene	$C_{10}H_{20}$	174°.9	0.7703
Margarylene	$C_{11}H_{22}$	195°.8	0.7822
Laurylene	$C_{12}H_{24}$	216°.2	0.7905

* Ber. der deutsch. chem. Gesellsch., 1883, p. 1873.

† Ibid., p. 1877.

‡ Proc. Amer. Acad., XXVII. 15.

As will be shown later, the specific gravity assigned by Warren to these constituents is very materially diminished by the removal of the aromatic hydrocarbons, and perhaps of other heavier bodies, that can only be separated by the application of more vigorous means of purification than Warrén applied.

DECANE, $C_{10}H_{22}$, 163°–164°.

When Pelouze and Cahours announced $C_{10}H_{22}$ as a constituent of Pennsylvania petroleum boiling at 160° ("sensiblement"), the presence in petroleum of the aromatic hydrocarbons had not been demonstrated, and since treatment with concentrated sulphuric acid and carbonate of soda was the sole means of purification, it is evident that their product must have still contained mesitylene, boiling point 163°, which, according to Engler, is contained in petroleum to the extent of 0.2 per cent. Then the specific gravity, 0.757 at 15°, assigned by them, is somewhat higher than that of this decane with mesitylene entirely removed. Warren did not observe the collection at this point of a distillate in any considerable quantity. But if, as it seems probable, Pelouze and Cahours investigated, not Pennsylvania, but Canadian petroleum, the close agreement between their specific gravity of decane at 160° with ours in Canadian petroleum is explained. In attempting to ascertain whether a hydrocarbon with this boiling point is present in Pennsylvania petroleum in any considerable amount, the distillates 150°–170° were carried through a long series of distillations, until several hundred grams collected between 158° and 162° under 730 mm., and finally more than 100 grams between 162° and 163° under 760 mm. One portion of this distillate was dried over sodium for analysis.

0.1453 gram of the oil gave 0.4560 gram CO_2, and 0.1865 gram H_2O.

	Calculated for		
	$C_{10}H_{22}$.	$C_{10}H_{20}$.	Found.
C	84.51	85.71	85.58
H	14.49	14.29	14.27

A determination of the specific gravity of this oil at 20° gave 0.7684. Its vapor density was determined by the Hofmann method in the vapor of aniline.

I. 0.1327 gram of the oil gave 66.8 c.c. of vapor at 182°, under a tension of 373.2 mm.

II. 0.1113 gram of the oil gave 59.5 c.c. of vapor at 182°, under a tension of 354.7 mm.

Calculated for $C_{10}H_{22}$.	Found. I.	II.
4.92	5.21	5.16

A portion of the same distillate was treated with fuming sulphuric acid with the aid of heat, and occasional agitation. When first added, a slight rise in temperature was observed, doubtless caused by the formation of mesitylene sulphonic acid. The acid was diluted, neutralized with baric carbonate, and the filtered solution evaporated nearly to dryness. A barium salt separated in clusters of needles, sparingly soluble in cold, more so in hot water. The quantity of this salt was too small for analysis. Another portion of the same distillate, with a mixture of nitric and sulphuric acids in the cold, formed an oily layer above the acids, which became solid on standing, and after crystallization from hot alcohol the needles that separated melted at 83°–84°; melting point of dinitromesitylene, 86°. When the dinitro product was warmed with fuming nitric acid, it formed prisms sparingly soluble in alcohol, and melting at 225°; melting point of trinitromesitylene, 230°. In the treatment with acids, 16 grams of the crude distillate gave 8 grams of the purified oil, with a loss of 50 per cent. When treated with fuming sulphuric acid, 16 grams of the crude product gave 9.5 grams pure oil, with a loss of 40 per cent. Mesitylene formed, therefore, a considerable proportion of the crude distillate. The purified oil had the faint odor characteristic of the pure petroleum hydrocarbons. After the removal of the hygroscopic moisture, the oil had no effect on bright metallic sodium. It gave upon analysis values required for decane: —

0.1644 gram of the oil gave 0.5084 gram CO_2, and 0.2284 gram H_2O.

	Calculated for $C_{10}H_{22}$.	Found.
C	84.51	84.34
H	15.49	15.44

The specific gravity of the purified oil at 20° was 0.7479, a value somewhat lower, as mentioned above, than that found by Pelouze and Cahours.*

Its vapor density was determined by the Hofmann method: —

0.1221 gram of the oil gave 68.5 c.c. of vapor at 182°, and under a tension of 352.8 mm.

Calculated for $C_{10}H_{22}$.	Found.
4.92	4.91

* Ann. Chim. Phys., (4.), I. 62.

Although the composition as shown by analysis seemed to be sufficient to demonstrate the presence of a hydrocarbon at this point, evidently analytical data alone would be insufficient, unless supported by a constant boiling point. The distillate used in the determinations described above was obtained after a long fractional separation, but without purification except the removal of sulphur compounds, until after the distillations were made. To prove beyond question the constancy in boiling point, another portion of the crude distillate after the fifteenth distillation was thoroughly agitated and warmed with fuming sulphuric acid, washed, dried, and the distillation continued fourteen times longer. About 100 grams of the oil collected so that it distilled at 163°–164°, mostly at 164°, under a tension of 760 mm., and with the mercury column all in the vapor. There seems therefore to be no reasonable doubt that Pennsylvania petroleum contains a decane with this boiling point. That this hydrocarbon is a decane is shown also by a determination of its molecular weight by the Beckmann method, which gave 142; and the formula $C_{10}H_{22}$ requires 142.

In forming the chlorine derivative of the hydrocarbon $C_{10}H_{22}$, boiling point 163°–164°, from Pennsylvania petroleum, 45 grams of the purified hydrocarbon was subjected to the action of chlorine in sunlight with a sheet of paper interposed, until it increased in weight 17 grams. The chlorine was delivered rapidly above the oil, and it was absorbed as fast as it could be added. Hydrochloric acid escaped with effervescence, and the rapidity of the reaction generated sufficient heat to maintain the temperature in the vicinity of 70°. With a slower stream of chlorine in other experiments the heat was dissipated without heating the oil, although the chlorine was as readily absorbed. Without further treatment, the chlorine product was subjected to fractional distillation *in vacuo* under tension of 80 mm. After ten distillations, approximately 6 grams collected at 125°–130°, which determinations of chlorine, carbon, and hydrogen showed to be monochlor decane: —

I. 0.2181 gram of the oil gave 0.5460 gram CO_2, and 0.2265 gram H_2O.

II. 0.2024 gram of the oil gave 0.1660 gram AgCl.

	Calculated for $C_{10}H_{21}Cl$.	Found. I.	II.
C	68.00	68.23	
H	11.90	11.55	
Cl	20.11		20.29

The specific gravity of this chlordecane at 20° was 0.8914. To the same product, separated by Pelouze and Cahours, no specific gravity was given. The chlordecanaphtene prepared by Markownikoff and Oglobine,* from decanaphtene boiling at 160°–162°, gave as its specific gravity 0.9390 at 0°. It boiled at 205°–206° (Cor.). Chlordecane obtained by Pelouze and Cahours boiled under atmospheric pressure at 200°–204°. Our chlordecane could not be distilled under atmospheric pressure without decomposition. As nearly as its boiling point could be determined, it distilled at 197°–203°.

On account of the small quantity of the chlorine derivatives described in this paper, the specific gravity determinations may not be strictly accurate. But the errors are doubtless small, and they do not affect the value of the determinations in establishing the identity of these derivatives.

In continuing the distillation of the higher chlorinated products from 163°–164° decane, Pennsylvania petroleum, approximately 15 c.c. of an oil collected after the eighth distillation at 160°–170° that was heavier than water. Even these high distillates, which could not be heated to their boiling points without decomposition, could be distilled *in vacuo* with little if any decomposition. This product gave on analysis the values required for dichlordecane: —

I. 0.2293 gram of the oil gave 0.4829 gram CO_2, and 0.1884 gram H_2O.

II. 0.2557 gram of the oil gave 0.3420 gram AgCl.

	Calculated for $C_{10}H_{20}Cl_2$.	Found. I.	II.
C	56.87	57.42	
H	9.48	9.13	
Cl	33.65		33.09

This dichlordecane gave 1.0187 as its specific gravity at 20°.

Decane, $C_{10}H_{22}$, 173°–174°.

Above 163° (730° mm.) the distillates were small in amounts to 168°, where they began to increase, and large quantities collected within degree limits to 173°, when they again fell off to small volumes. The fraction 169°–170° was selected for examination, which included analysis of the crude distillate, analyses after purification with acids, and the

* Ann. Chim. Phys., (6.), II. 453.

formation of the chlorine derivatives. It is interesting to note that, without purification, unpurified distillates give percentages of carbon and hydrogen that correspond to the series C_nH_{2n}, or to numbers between this series and the series C_nH_{2n+2}. The unpurified distillate 169°–170° (730 mm.) gave the following results: —

0.1521 gram of the oil gave 0.4758 gram CO_2, and 0.2018 gram H_2O.

	Calculated for $C_{10}H_{22}$.	Calculated for $C_{10}H_{20}$.	Found.
C	84.51	85.71	85.31
H	15.49	14.29	14.72

The specific gravity of this distillate at 20° was found to be 0.7502. Its vapor density, determined by the Hofmann method, gave the following value: —

0.1533 gram of the oil gave 74.6 c.c. of vapor at 182°, under a tension of 414.6 mm.

Calculated for $C_{10}H_{22}$.	Found.
4.92	4.86

Evidently no particular value can be attached to such determinations of vapor density, since, as shown by analysis, the oil is not composed of a single body. The same is true of boiling points unsupported by other values. The contaminating body frequently has the same or nearly the same boiling point as the principal constituent, and after the removal of the impurity the boiling point is not materially changed. Another portion of the crude distillate was shaken with ordinary strong sulphuric acid washed with caustic soda water, and dried with sodium.

I. 0.1476 gram of this oil gave 0.4586 gram CO_2, and 0.1980 gram H_2O.
II. 0.1674 gram of this oil gave 0.5190 gram CO_2, and 0.2263 gram H_2O.

	I.	II.
C	84.72	84.57
H	14.90	15.03

The specific gravity of this oil was 0.7486. Its vapor density was determined; 0.1454 gram of the oil gave 73 c.c. of vapor at 182°, under a tension of 410 mm.

Calculated for $C_{10}H_{22}$.	Found.
4.92	4.75

Another portion of the crude distillate was agitated with a mixture of nitric and sulphuric acids. An oily nitro product separated above the acids, which became partially crystalline on standing. It was doubtless a nitro derivative of cymol; boiling point of metacymol 174°–176°, of paracymol 171°–172°.

The quantity of the nitro product was small, and the proportion of cymol was still further shown to be very small by treatment with fuming sulphuric acid. 185 grams of the distillates 167°–170°, after the eighteenth distillation, first by agitation in the cold, and then by warming to 125°, gave a loss in weight of only 15 grams, or about 8 per cent of the weight taken. A barium salt was formed of the sulphonic acid, but it appeared as a thick gummy mass, so uninviting that nothing further was done with it. The purification with fuming sulphuric acid was intended more especially to show whether the boiling point of the distillates would be materially affected. But the only difference observed was that they came together more readily and completely within one degree, 169°–170° under 730 mm., and at 173°–174°, chiefly at 174°, under a tension of 760 mm., with the mercury column all in the vapor. It is interesting to observe how slightly the boiling point was affected by the removal of the contaminating bodies. Evidently, the principal influence of the latter was in preventing the hydrocarbon from collecting closely at its true boiling point.

The remaining oil was boiled with sodium as long as the metal was affected, and until it remained unchanged on standing with the oil. Even after this treatment was repeated several times, the percentage of carbon was somewhat too high and hydrogen too low: —

0.1503 gram of the oil gave 0.4664 gram CO_2, and 0.2050 gram H_2O.

	Calculated for $C_{10}H_{22}$.	Found.
C	84.51	84.65
H	15.49	15.14

After this purification the specific gravity obtained was 0.7475. For still further certainty as to the purity and composition of this distillate another portion was warmed during several hours with fuming sulphuric acid and shaken thoroughly. After washing and standing over sodium, it was analyzed: —

0.1754 gram of the oil gave 0.5431 gram CO_2, and 0.2442 gram H_2O.

	Calculated for $C_{10}H_{22}$.	Found.
C	84.51	84.45
H	15.49	15.47

In the latter treatment the acid solution when neutralized with baric carbonate gave a barium salt in clusters of needles, sparingly soluble in water, doubtless the barium salt of cymol-sulphonic acid, although the quantity obtained was too small for analysis.

After this prolonged treatment with the fuming acid, the specific gravity was found to be 0.7467, substantially the same as in the previous determinations, and practically the same as the specific gravity of the decane boiling at 163°.

The molecular weight of this hydrocarbon, as determined by the Beckmann method, using benzol as a solvent, was found to be 144; since the formula $C_{10}H_{22}$ requires 142, this determination leaves no doubt that this body is decane, and not a higher homologue.

The chlorine derivatives of the decane 173°–174° were formed in the same manner as those of its isomer. 32 grams of the purified distillate was allowed to absorb 9 grams of chlorine, and the product was fractioned *in vacuo*. After the fourth distillation a small quantity collected at 130°–140°, which gave percentages of carbon, hydrogen, and chlorine required for monochlordecane: —

I. 0.2082 gram of the product gave 0.1699 gram AgCl.
II. 0.2003 of the product gave 0.5038 gram CO_2, and 0.2150 gram H_2O.

	Calculated for $C_{10}H_{21}Cl$.	Found. I.	Found. II.
C	68.00		68.61
H	11.90		11.93
Cl	20.11	20.19	

The specific gravity of this chlordecane at 20° was 0.8874, a value somewhat lower than the specific gravity of the chlordecane formed from 163° decane, 0.8914. After the study of its other properties not enough of this chlordecane remained for a determination of its boiling point under atmospheric pressure. As the specific gravity of the chlorine derivative of petroleum decane, Lemoine * gave 0.908. This value must have been obtained from decane boiling at 162°, since the French chemists have never recognized a decane in petroleum boiling at 173°. It was probably obtained in an impure product, since it is very considerably higher than our determination, which was made, as already shown, in chlordecane from well purified decane.

In continuing the vacuum distillation of the chlorine products from

* Bull. Soc. Chim., XLI. 165.

173° decane, a considerable quantity collected at 170°–171°, 80 mm., which distilled at 235°–240°, 747 mm. Its composition was shown by analysis: —

0.2008 gram of the oil gave 0.4121 gram CO_2, and 0.1641 gram H_2O.
0.2540 gram of the oil gave 0.3532 gram AgCl.

	Calculated for $C_{10}H_{20}Cl_2$.	Found. I.	II.
C	56.87	55.96	
H	9.48	9.08	
Cl	33.65		34.38

This substance is, therefore, a dichlordecane. The quantity of the dichlordecane was barely sufficient for a determination of its specific gravity; it gave at 20°, 1.0126.

The presence of a decane at 174° seems therefore to be established in Pennsylvania petroleum, confirming the observations of Warren, who alone of all those who have examined American petroleum found a body at this point. If Pelouze and Cahours had carried their course of distillations sufficiently far, they could not have failed to discover this body, since it forms such a large proportion of the higher boiling petroleum distillate. Those chemists did, however, collect a distillate at 180°–182° which gave analytical values and a vapor density very closely supporting the formula $C_{11}H_{24}$. For some time I was in doubt as to whether a distillate might not persist at this point, and it was only after a prolonged series of separations that it was possible to separate the distillates 180°–182° entirely into higher and lower limits, thus supporting the conclusion of Warren, that Pennsylvania petroleum contains no hydrocarbon in appreciable quantity boiling in the vicinity of 180°.

Hendecane, $C_{11}H_{24}$, 196°.

With increasing boiling points the distillates showed less stability, as indicated by more color in the residue in a long course of distillations, although this was not sufficient to interfere with the collection of a homogeneous body within narrow limits of temperature. Between 189° and 192° distillates early began to accumulate, and the quantity gradually increased until 150 c.c. was obtained which distilled entirely at 190°–191° under 730 mm.

On standing over sodium, a portion of this distillate deposited a reddish flocculent precipitate in very appreciable quantity, which indeed was

observed in all unpurified distillates. On this account very little importance has been attached to the composition of these oils as shown by analysis, except to demonstrate what slight weight can be given to those results. Drying with sodium is indispensable, on account, as shown in another connection, of the difficulty in removing water by other means.

Determinations of carbon and hydrogen in the crude distillate 190°–191° dried over sodium gave the following results: —

0.1521 gram of the oil gave 0.4787 gram CO_2, and 0.1972 gram H_2O.

	Calculated for C_nH_{2n}.	Found.
C	85.71	85.82
H	14.29	14.41

The specific gravity at 20° was found to be 0.7673. After thorough agitation with sulphuric acid and washing with sodic hydrate and water, the specific gravity was scarcely affected, 0.7662.

A comparison of the composition and specific gravity of the crude distillate 190°–191°, 730 mm., as shown above, with the results of Warren and of Pelouze and Cahours, in connection with what follows after further purification, reveals the cause of the lack of uniformity in the earlier work. The specific gravity of Warren's analyzed product, 0.7721 at 15°, which was only purified by boiling with sodium, is substantially the same as that of Pelouze and Cahours, 0.7780 at 20°, which was purified with concentrated sulphuric acid and sodic carbonate, but appreciably higher than the specific gravity of our crude distillate, only dried over sodium. The percentage composition of these products purified in this manner may be more clearly understood if the results of analysis are brought together, as in the following table: —

	Warren. I.	Warren. II.	Mabery.	Pelouze and Cahours. I.	Pelouze and Cahours. II.
C	85.60	85.33	85.82	84.79	84.58
H	14.80	14.65	14.41	15.42	15.36

Required for

	$C_{11}H_{22}$.	$C_{11}H_{24}$.	$C_{12}H_{26}$.
C	85.72	84.62	84.70
H	14.29	15.38	15.30

It is difficult to see how results so closely supporting the formula C_nH_{2n+2} as those of Pelouze and Cahours could be obtained in a product still containing aromatic hydrocarbons, as shown by their method

of purification and by the higher specific gravity. In the case of this particular hydrocarbon, the method of purification is not especially mentioned, but their general method, which is mentioned under nearly every other member of the long series of hydrocarbons which they examined, consisted in agitating the oil in the cold with concentrated sulphuric acid and washing with sodic carbonate. Then their method included no special means of drying the oil for analysis. It is quite impossible to remove moisture entirely from these hygroscopic oils without the aid of the most vigorous desiccating agents. Nothing less than standing continuously over sodium, in my experience, will insure a perfectly dry condition.

It is evident from the following description of their experiments that Pelouze and Cahours tried the action of reagents on their oil, although they seem not to have suspected the presence of an aromatic hydrocarbon C_nH_{2n-6}: "Le brome, l'acide azotique fumant, l'acide sulfurique au maximum de concentration, l'acide azotique de Nordhausen ne l'attaquent pas à froid. Le mélange des acides azotique et sulfurique agit sur le carbure lorsqu'on maintient ces corps pendant quelque temps en ébullition. Prolonge l'on l'action, on voit se former une petite quantité d'un produit solide et cristallisable. Il se sépare en même temps une huile jaunâtre un peu plus dense que l'eau. De plus, on démèle dans les vapeurs nitreuses l'odeur caractéristique des acides volatils homologues de l'acide acétique."

Upon agitation with nitric and sulphuric acids, the distillate 190°–191° deposited a heavy nitro compound.

Our observations concerning the action of a mixture of concentrated nitric and sulphuric acids in the cold on this distillate do not coincide with those of Pelouze and Cahours. Immediately upon vigorous agitation, a heavy nitro compound separated as a heavy oil, forming a crystalline product on standing. 20 grams of the oil lost 4.5 grams by this treatment, equivalent to 22 per cent of its weight. The nitro compound was very sparingly soluble in hot alcohol, from which it crystallized in needles, melting at 169°–170°. As will be seen later, nitro compounds with the same melting point were separated from Ohio and Canadian petroleum, which do not correspond in melting point to that of either dinitrodurol, 205°, nor of dinitroisodurol, 156°, although crystallization was continued until the melting point was pretty constant. It would have been interesting to obtain sufficient of this substance for more complete examination; but, with the great amount of work on hand in connection with the principal hydrocarbons, it did not seem best to allow our

attention to be diverted from the main object in view. It should not be understood that the diminution in weight mentioned above on treating with acids was due entirely to the removal of aromatic hydrocarbons. In all the petroleum hydrocarbons we have separated, on treating with nitric and sulphuric acids, a large proportion of the products has remained in solution, and it has been possible to reduce them only very slowly by heating with sodium. From the distillates above 150°, heavy dark brown precipitates have been formed at first, followed by light flocculent deposits resembling aluminic hydrate. On distilling after treating with sodium, usually a considerable residue is left. If heating with sodium be continued until there is no further action, the metal will remain bright in the oil, and we have looked on this as an indication of purity.

The oil separated from the acid mixture was boiled with sodium until it produced no further decomposition, shaken with sulphuric acid, and allowed to stand a long time in contact with sodium. Since the metal remained unaffected, the oil was assumed to be completely purified; nevertheless, analysis showed still remaining a trace of the less hydrogenized body: —

0.1547 gram of the oil gave 0.4816 gram CO_2, and 0.2104 gram H_2O.

	Calculated for $C_{11}H_{24}$.	Found.
C	84.63	84.87
H	15.38	15.12

A determination of the specific gravity of the purified oil gave 0.7585.

To prove with greater certainty the composition of this hydrocarbon, the crude distillate obtained as described above was heated on the steam bath with fuming sulphuric acid, which gave some decomposition, and the oil remaining washed thoroughly with caustic soda and water. 20 grams of the crude distillate gave 16.5 grams of the purified oil, with a loss of 17.5 per cent, which is probably an approximate measure of the proportion of aromatic hydrocarbons in this distillate. It is probable that the loss in weight with the mixture of nitric and sulphuric acids included some decomposition of the principal hydrocarbon. The oil treated with fuming sulphuric acid was carried through ten distillations, after which it collected for the most part within one degree, and 100 grams distilled at 196°–197°, under 760 mm., and with the mercury column all in the vapor. This product was again warmed with fuming sulphuric acid, washed, and dried over sodium.

In the latter experiment the acid was only slightly discolored. The

oil gave the faint characteristic odor of these hydrocarbons, which is easily recognized when the impurities are removed. It then gave percentages of carbon and hydrogen required for a hydrocarbon of the series C_nH_{2n+2}.

I. 0.1502 gram of the oil gave 0.4665 gram CO_2, and 0.2090 gram H_2O.

II. 0.1661 gram of the oil gave 0.5157 gram CO_2, and 0.2322 gram H_2O.

	Calculated for $C_{11}H_{24}$.	Found. I.	II.
C	84.62	84.70	84.67
H	15.38	15.46	15.53

The specific gravity of the oil 196°–197°, after purification in this manner, was found to be 0.7581. The close agreement in specific gravity of the products after treatment with the mixture of nitric and sulphuric acids, and with fuming sulphuric acid, as well as the proportions of carbon and hydrogen, indicate that the oil was quite thoroughly purified.

That the formula of the purified hydrocarbon boiling at 196° is $C_{11}H_{24}$, and not the next higher homologue, receives further support by a determination of its molecular weight, in which Mr. Hudson obtained, by the Beckmann method, the value 157, required for $C_{11}H_{24}$, 156.

In the preparation of the chlorine derivatives of the hydrocarbon $C_{11}H_{24}$, boiling point 196°, Pennsylvania petroleum, 40 grams of the oil was allowed to absorb 14 grams of chlorine, and the chlorine product was fractioned *in vacuo*. After five distillations, 10 c.c. collected at 145°–150° (80 mm.), that distilled with decomposition at 225°–230°, bar. 747 mm. This product gave on analysis percentages of carbon, hydrogen, and chlorine required for $C_{11}H_{23}Cl$: —

I. 0.2291 gram of the substance gave 0.1713 gram AgCl.

II. 0.1933 gram of the substance gave 0.4914 gram CO_2, and 0.2071 gram H_2O.

	Calculated for $C_{11}H_{23}Cl$.	Found. I.	II.
C	69.29		69.30
H	12.07		11.91
Cl	18.13	18.49	

The specific gravity of monochlorhendecane at 20° was found to be 0.8721. Pelouze and Cahours found that the hydrocarbon which they

collected at 196°–200° absorbed chlorine at a gentle heat with the formation of a monochlor derivative that boiled at 242°–245° with a specific gravity of 0.9330 at 22°. These values are much in excess of the determinations given above. Our boiling point under atmospheric pressure was only approximate, since the chlorine product was considerably decomposed at those temperatures. In the action of chlorine, the substitution proceeded with the greatest readiness as soon as the chlorine came in contact with the hydrocarbon. No heat was necessary, although, if the action proceeded rapidly, much heat was developed.

The composition of the product obtained by Pelouze and Cahours corresponds to the formula $C_{12}H_{25}Cl$, as shown by the following record of their analyses: —

	Calculated for $C_{12}H_{25}Cl$.	Found
C	70.41	70.34
H	12.23	12.37
Cl	17.36	17.53

In further support of the formula $C_{11}H_{23}Cl$, Mr. Hudson made a determination of the molecular weight of the chloride by the Beckmann method, using benzol as a solvent, in which he obtained 191; the formula $C_{11}H_{23}Cl$ requires 190.

Evidently a dichlorhendecane was also formed in this chlorination, since in the vacuum distillation, about 5 c.c. collected at 190°–200°, that gave a percentage of chlorine two per cent too low for the required value. But the quantity was too small to purify it sufficiently to give acceptable results.

Dodecane, $C_{12}H_{26}$, 214°–216°.

Above 193°, 730 mm., the fractions were very small to 208°, but between 208° and 210° much larger quantities collected, for the most part at 209° to 210°. Without further purification except drying with sodium, the crude distillate was analyzed: —

0.1392 gram of the oil gave 0.4355 gram CO_2, and 0.1845 gram H_2O.

	Calculated for C_nH_{2n}.	Found.
C	85.71	85.33
H	14.29	14.73

A determination of its specific gravity gave 0.7745. After treatment with concentrated sulphuric acid, the specific gravity was not changed, — 0.7744. Another portion of the crude distillate was shaken with nitric

and sulphuric acids, and allowed to stand several hours. After separation from the small quantity of the heavy nitro product and the acid, the oil was boiled with sodium until there was no further action, and the metal remained unaffected on standing several weeks. The oily nitro product deposited a small quantity of crystals on standing, but not enough to purify for a determination of its melting point.

Purified in this manner, this distillate gave the following results on analysis : —

I. 0.1547 gram of the oil gave 0.4816 gram CO_2, and 0.2104 gram H_2O.
II. 0.1474 gram of the oil gave 0.4562 gram CO_2, and 0.2017 gram H_2O.

	Calculated for $C_{12}H_{26}$.	Found. I.	II.
C	84.72	84.87	84.41
H	15.28	15.12	15.21

Its specific gravity at 20° was found to be 0.7684.

Another portion of the crude fraction 209°–210°, purified by thorough agitation and warming with fuming sulphuric acid, twice repeated, gave the following results on analysis : —

0.1471 gram of the oil gave 0.4537 gram CO_2, and 0.2068 gram H_2O.

	Calculated for $C_{12}H_{26}$.	Found.
C	84.72	84.12
H	15.28	15.63

The specific gravity of the oil after treatment with the fuming acid was 0.7729, somewhat higher than the portion purified with nitric and sulphuric acids. It is quite possible that the purification with fuming sulphuric acid, in this instance, was not capable of removing the contaminating bodies as thoroughly as the other method. The purified hydrocarbon was found to distil completely at 214°–216°, under a tension of 760 mm., and with the mercury column all in the vapor. A determination of its molecular weight by the Beckmann method gave Mr. Hudson 173; required for the formula $C_{12}H_{26}$, 170.

In the formation of the chlorine derivatives from the hydrocarbon $C_{12}H_{26}$, Pennsylvania petroleum, 95 grams of the purified hydrocarbon was exposed to the action of chlorine until 30 grams was absorbed. Apparently chlorine substitutes as readily in the hydrocarbons of higher,

as in those of lower boiling points. In fractioning under 80 mm. after six distillations, about 20 c.c. collected at 142°–153°, which distilled at 230°–235° atmospheric pressure. In none of the distillates of chlorine derivatives was hydrochloric acid detected as a product of decomposition when distilled *in vacuo.* Under atmospheric pressure it was impossible to carry on these distillations without serious decomposition. The composition of this fraction corresponded to that of $C_{12}H_{25}Cl$.

I. 0.1910 gram of the oil gave 0.1385 gram AgCl.

II. 0.1339 gram of the oil gave 0.3434 gram CO_2, and 0.1423 gram H_2O.

	Calculated for $C_{12}H_{25}Cl$.	Found. I.	Found. II.
C	70.42		69.93
H	12.23		11.81
Cl	17.36	17.93	

In determining the specific gravity of this chlorine derivative at 20°, it gave 0.8919. A determination of its molecular weight by the Beckmann method, with benzol as a solvent, gave Mr. Hudson 200; required for $C_{12}H_{25}Cl$, 204. The chloride formed by Pelouze and Cahours from their distillate 216°–218° boiled at 258°–260°, somewhat higher than the boiling point of the chloride described in this paper. From the results of their analyses, they deduced the formula $C_{13}H_{27}Cl$.

The chlorination of this product was not carried far enough to form sufficient of the dichlor derivative to separate it by distillation. The greater part of the oil after chlorination distilled at 212°–214°, the boiling point of the hydrocarbon.

A description of these experiments, which are intended to establish the composition of the hydrocarbon distilling at 214°–216°, should not be concluded without a statement of the relation they sustain to those of Warren and of Pelouze and Cahours, the only experimenters who have hitherto attempted the separation of this constituent from American petroleum. The two determinations most nearly concerned in this discussion are specific gravity and percentage composition. In the following comparison of specific gravity determinations and percentage composition, it should be borne in mind that Warren purified his distillate only by boiling with metallic sodium, Pelouze and Cahours by agitation with concentrated sulphuric acid and washing with sodic carbonate; with those results are brought together the determinations described in this paper in the crude distillate, after agitation with concentrated sulphuric acid, and after more thorough purification with the acid mixture: —

	Warren, 15°.		Pelouze & Cahours, 20°.		Mabery, 20°. Crude Distillate.	Agitation with H_2SO_4.	Purified.	
Sp. gr.	0.7804		0.7960		0.7745	0.7744	0.7684	
	I.	II.	I.	II.			I.	II.
C	84.66	85.74	84.58	84.51	85.33		84.87	84.41
H	14.85	14.66	15.37	15.45	14.73		15.12	15.21

The percentages of carbon and hydrogen required for the formula $C_{12}H_{26}$ are, C 84.72, H 15.30; for the formula $C_{13}H_{28}$, C 84.78, H 15.22. Evidently the differences in percentage composition are not sufficient to distinguish by analysis alone which of the two formulas is the correct one. But the differences between either of these formulas and the formula $C_{12}H_{24}$, C 85.71, H 14.29, should be readily shown by analysis.

Having at hand a portion of the purified distillate 214°–216° that had been treated with chlorine and the part not chlorinated distilled, I continued the distillation until the chlorine derivatives were completely removed, and the hydrocarbon was treated with fuming sulphuric acid and distilled over sodium. It then gave as its specific gravity 0.7729, substantially the same as before chlorination. Normal dihexyl prepared by the action of zinc and hydrochloric acid on normal hexyl iodide boils at 214°.5 and apparently is identical with a hydrocarbon having the same composition, obtained by electrolysis of potassium œnanthylate (Schorlemmer). The latter has the specific gravity 0.7738 at 17°. It is therefore probable that the hydrocarbon $C_{12}H_{26}$, boiling at 214°–216°, from American petroleum, has the same form. The purified hydrocarbon then gave the following percentages of carbon and hydrogen: —

I. 0.1599 gram of the oil gave 0.4978 gram CO_2, and 0.2177 gram H_2O.
II. 0.1617 gram of the oil gave 0.5021 gram CO_2, and 0.2270 gram H_2O.
III. 0.1559 gram of the oil gave 0.2193 gram H_2O. The CO_2 was lost.

	Calculated for $C_{12}H_{26}$.	Found. I.	II.	III.
C	84.72	84.89	84.69	
H	15.28	15.10	15.31	15.63

These results indicate the absence of any impurity not readily acted on by chlorine.

As one of the results of this examination it can, I think, be safely asserted that the constituents of Pennsylvania petroleum with boiling points at 163°–164°, 173°–174°, 196°–197°, and at 215°–216°, constitute

the main body of this petroleum within these limits, and whatever other bodies may be present, they are to be found only in comparatively small quantities. As to the proportion of aromatic hydrocarbons in the crude oil, no direct estimation can be based on these observations.

Fuming sulphuric acid removed 40 per cent of the crude distillate 160°–161°, leaving decane as the remaining 60 per cent. Whether the portion removed was mesitylene alone may be questionable, but no doubt it formed the larger part of the body uniting with the fuming acid. Even in such prolonged fractional separations as those described in this paper, it cannot be assumed that nearly all the decane 163°–164° was collected in the fractions which should contain it, neither is it probable that the crude distillate from which was selected the specimen for the separation of these constituents contained all the decane in the corresponding quantity of crude oil. But it is evident that the aromatic hydrocarbons are present in no inconsiderable amounts, and without doubt these bodies have much influence on the illuminating qualities of the oil. As shown by the slight changes in specific gravity after the action of ordinary concentrated sulphuric acid, the action of this acid in the usual method of refining does not include to any considerable extent the removal of the aromatic hydrocarbons. Its beneficial action seems to concern more especially the decomposition products of distillation and certain constituents present in minute quantities, such as the unsaturated hydrocarbons, the oxygen, and nitrogen compounds. It scarcely need be mentioned that this applies to the action of sulphuric acid in the cold. When heated, without doubt a part of the aromatic hydrocarbons would be removed, to the detriment of the burning qualities. The formation of barium salts from all the distillates treated with fuming sulphuric acid proves the presence in appreciable amounts of a wide range of aromatic hydrocarbons.

Without reference to the percentages of carbon and hydrogen, the low specific gravity of the hydrocarbons described above is sufficient to show that they are not naphtenes. The following comparison of the unpurified distillates and the purified hydrocarbons as regards their specific gravity with the naphtenes separated by Markownikoff from the Russian oil will perhaps make these differences more clearly understood.

Baku naphtenes: —

	B. P.	Specific Gravity.
$C_{10}H_{20}$	160°–162°	0.795 (0°)
$C_{11}H_{22}$	180°–182°	0.8119 (0°)
$C_{12}H_{24}$	196°–197°	0.8055 (14°)

Pennsylvania C_nH_{2n+2}: —

	B. P.	Specific Gravity at 20°. Purified.	Unpurified.
$C_{10}H_{22}$	163°–164°	0.7479	0.7684
$C_{10}H_{22}$	173°–174°	0.7467	0.7502
$C_{11}H_{24}$	196°–197°	0.7581	0.7673
$C_{12}H_{26}$	214°–216°	0.7676	0.7745

Another important result of this study is the evidence that the main body of the hydrocarbons in Pennsylvania petroleum within these limits of temperature are members of the series C_nH_{2n+2}. Satisfactory analytical data in proof of this conclusion have cost a vast expenditure of time and effort, not only in the routine labor of separation and purification, but in obtaining sufficiently close percentages of carbon and hydrogen. In such a large number of determinations the ordinary method of combustion becomes exceedingly tedious, since all details must be watched with the greatest care. In the beginning of analysis there was not the slightest evidence as to whether the hydrocarbons were of the series C_nH_{2n+2}, or of the series C_nH_{2n}. The extreme hygroscopic nature of these bodies was not then appreciated, nor the refinement in purification necessary to yield acceptable results. Many analyses were made before these details were fully understood.

Constituents of Ohio Trenton Limestone Petroleum.

The constituents of Ohio petroleum between 160° and 216° were sought for in vacuum distillates obtained from the crude oil, as described in a former paper.*

Distillation *in vacuo* was continued until all portions had collected that could be brought together within the desired limits. Further concentration was carried on under atmospheric pressure, since this did not occasion serious decomposition. Probably no petroleum distillates with such high boiling points can entirely escape decomposition in a long course of distillations, but small amounts of decomposition products can no doubt be removed by sulphuric acid, leaving the main body of the oil free from contamination. After the first distillations *in vacuo* Ohio distillates seem to suffer no more change during distillation than those from Pennsylvania oil. Before separation into two degree fractions, the sulphur compounds were removed so far as possible by precipitation with mercuric chloride. As the distillation proceeded, the characteristic

* Proc. Amer. Acad., XXXI. 25.

"heaps" began to appear in the vicinity of 160°, 730 mm., falling off below 158° and above 163°. These portions were therefore carried through a long course of separations, fifty altogether, forty-five within one degree, after which they collected mainly at 159°–162°. A combustion of the crude distillate 159°–160°, purified as explained above only by mercuric chloride, gave the following results: —

I. 0.1591 gram of the oil gave 0.4983 gram CO_2, and 0.2076 gram H_2O.

	Calculated for $C_{10}H_{20}$.	Calculated for $C_{10}H_{22}$.	Found.
C	85.71	84.51	85.41
H	14.29	15.49	14.50

On the basis of these values alone, there should be no hesitation in assigning to this oil the formula $C_{10}H_{20}$. The specific gravity of this distillate was found to to be 0.7717. Its vapor density was determined by the Hofmann method: —

0.1272 gram of the oil gave 67 c.c. of vapor at 182°, and under a tension of 374.4 mm.

Calculated for $C_{10}H_{22}$.	Found.
4.92	4.96

After treatment with ordinary concentrated sulphuric acid, another portion of this distillate gave 0.7678 as its specific gravity, and the following percentages of carbon and hydrogen: —

0.1416 gram of the oil gave 0.4452 gram CO_2, and 0.1855 gram H_2O.

C	85.76
H	14.56

Agitation of the crude distillate in the cold with a mixture of concentrated nitric and sulphuric acids caused the separation of a heavy oil that deposited crystals of a nitro product on standing. After crystallization from hot alcohol, in which it is sparingly soluble, this substance melted at 229°, showing it to be trinitromesitylene, melting point 230°–232°. Complete removal of the nitro compound from decane required prolonged boiling with sodium followed by agitation with sulphuric acid. The hydrocarbon then no longer attacked the metal, nor tarnished it on long standing. Purified in this manner, this oil gave values required for decane: —

0.1512 gram of the oil gave 0.4677 gram CO_2, and 0.2088 gram H_2O.

	Calculated for $C_{10}H_{22}$.	Found.
C	84.51	84.35
H	15.49	15.35

For further assurance as to the composition of this hydrocarbon, another portion of the crude distillate was first agitated in the cold with fuming sulphuric acid, which produced no heat, and then heated with the acid on the steam bath. As in most of the crude oils when treated in this manner, the acid turned dark when heated, and evidently extracted a considerable proportion of the oil. After washing with sodic hydrate and water, the remaining oil gave only the faint odor characteristic of the petroleum hydrocarbons. In many of the analyses, it will be seen that the percentage of hydrogen is somewhat lower than should be expected in a pure substance. This deficiency is doubtless due to a very small proportion of the hydrocarbon with less hydrogen, the last traces of which it is somewhat difficult to remove. The fraction 160°–162°, after the last purification, contained the following percentages of carbon and hydrogen : —

0.1532 gram of the oil gave 0.4740 gram CO_2, and 0.2113 gram H_2O.

	Calculated for $C_{10}H_{22}$.	Found.
C	84.51	84.38
H	15.49	15.33

A determination of its specific gravity at 20° gave 0.7535, a value slightly higher than the specific gravity of the corresponding fraction of the Pennsylvania oil, doubtless due to the slight trace of impurity still remaining. In determining the molecular weight of this decane by the method of Beckmann, Mr. Hudson obtained 145 ; required for $C_{10}H_{22}$, 142.

The boiling point of this hydrocarbon, so thoroughly purified that neither fuming nitric acid nor fuming sulphuric acid produced further change, was found to be nearly the same as that of 163° decane from Pennsylvania petroleum. 50 c.c. distilled entirely between 162°.5 and 163°.5 under a barometric pressure of 757.5 mm.

Since even a larger proportion of the crude distillate was removed in combination with fuming sulphuric acid than from the Pennsylvania distillate 163°, an attempt was made to ascertain the composition of the barium salt, formed by neutralizing with baric carbonate and crystallizing the filtered solution, after boiling with bone black. A considerable

quantity of the barium salt crystallizing in needles was obtained, and the percentage of barium found, 25.95, agreed closely with the theoretical percentage of barium in barium mesitylene sulphonate $(C_9H_{11}SO_3)_2Ba$, 25.61. But the salt proved to be anhydrous, while according to Jacobson,* barium mesitylene sulphonate crystallizes with 9 H_2O. On account of the limited supply of the barium salt, it was not possible to verify this determination by further study; but there can be no doubt of the possibility of forming a barium salt of mesitylene sulphonic acid in this manner, since trinitromesitylene melting at 225°–230°, melting point of trinitro mesitylene, 230°, was formed without difficulty by the action of fuming nitric acid on this distillate.

As further evidence of the composition of the hydrocarbon 163° Ohio petroleum, 46 grams well purified with fuming sulphuric acid was exposed to the action of chlorine until the weight had increased 11 grams. The chlorinated product was fractioned twelve times under 80 mm., when 15 c.c. collected at 130°–135°, distilling at 200°–208° atmospheric pressure. It was shown by analysis to have the composition required for $C_{10}H_{21}Cl$.

I. 0.2340 gram of the substance gave 0.1934 gram AgCl.

II. 0.1935 gram of the substance gave 0.4785 gram CO_2, and 0.2119 gram H_2O.

III. 0.1715 gram of the oil gave 0.4246 gram CO_2, and 0.1963 gram H_2O.

	Calculated for $C_{10}H_{21}Cl$.	Found. I.	II.	III.
C	68.00		67.44	67.53
H	11.90		12.17	12.73
Cl	20.11	20.45		

In a determination of its specific gravity at 20°, this chlordecane gave 0.8958. In continuing the distillation of the chlorine product after the twelfth fraction, 10 c.c. collected at 160°–170°, specific gravity, 1.0627 at 20°, which gave the percentages of carbon, hydrogen, and chlorine required for $C_{10}H_{20}Cl_2$.

I. 0.2984 gram of the substance gave 0.4105 gram AgCl.

II. 0. 2753 gram of the substance gave 0.5746 gram CO_2, and 0.2356 gram H_2O.

	Calculated for $C_{10}H_{20}Cl_2$.	Found. I.	II.
C	56.87		56.94
H	9.47		9.51
Cl	33.65	34.03	

* Ann. Chem. Pharm., XLVI. 95.

NORMAL DECANE, B. P. 173°–174°.

Above 162° (730 mm.), the distillates were small to 168°. After long continued distillation, 300 grams collected at 169°–170° (730 mm.), which, without further purification, except drying over sodium, gave the following percentages of carbon and hydrogen: —

I. 0.1434 gram of the oil gave 0.4486 gram CO_2, and 0.1927 gram H_2O.
II. 0.1577 gram of the oil gave 0.4948 gram CO_2, and 0.2070 gram H_2O.

	Calculated for		Found.	
	$Cl_{10}H_{23}$.	$Cl_{10}H_{20}$.	I.	II.
C	84.51	85.71	85.33	85.55
H	15.49	14.29	14.94	14.58

A determination of the specific gravity of this distillate gave 0.7621, a value considerably higher than that of the corresponding unpurified Pennsylvania distillate, 0.7502.

0.1670 gram of the oil gave 79 c.c. of vapor at 182°, under a tension of 366 mm.

Calculated for $C_{10}H_{22}$.	Found.
4.90	5.15

A portion of the crude distillate was shaken with concentrated sulphuric acid, washed, and dried for analysis: —

0.1504 gram of the oil gave 0.4708 gram CO_2, and 0.1984 gram H_2O.

C	85.37
H	14.67

The specific gravity of this oil after treatment with sulphuric acid was somewhat lower than that of the crude distillate, 0.7580. A determination of its vapor density gave 5.02. The fraction 169°–170°, Ohio oil, was the first to be submitted to the action of the mixture of nitric and sulphuric acids. When a small quantity of the oil was heated to about 125° during 24 hours with the acid mixture, nitrous fumes were freely evolved and the volume of the oil gradually diminished until very little remained. Upon diluting the acid, a heavy, tarry mass was precipitated, evidently a product of decomposition of the hydrocarbon. In another experiment, 25 grams of the crude distillate were agitated in the cold with the acid mixture, separated from the acid and the oily nitro product, washed, and dried. After boiling with sodium and shaking with sulphuric acid, there

remained of the quantity taken 17 grams, with a loss of 32 per cent. A portion of the nitro product crystallized on standing, and after several crystallizations from hot alcohol, in which it was sparingly soluble, the melting point could not be raised above 164°–165°. In testing the action of sulphuric acid alone on the distillate 171°–172°, 25 grams of the crude oil was agitated with three successive portions of concentrated sulphuric acid, washed with sodic hydrate and water, and dried. In the first treatment, in which the oil lost in weight 1.8 grams, the acid was badly discolored; the subsequent portions were not affected. The oil was next heated gently with fuming sulphuric acid with agitation, which caused considerable blackening, washed first with concentrated sulphuric acid, then with sodic hydrate and water, and dried. After the last treatment, the oil weighed 19.8 grams, with a loss of 25 per cent.

It is evident from these observations that some care is necessary in attempting to purify these hydrocarbons with concentrated nitric acid. In the cold or under a gentle heat not prolonged, the decomposition is probably not serious. But at higher temperatures, as shown above, the action may proceed too far. The purified oil gave satisfactory results on analysis : —

I. 0.1373 gram of the oil gave 0.4247 gram CO_2, and 0.1900 gram H_2O.

II. 0.1459 gram of the oil gave 0.4520 gram CO_2, and 0.2090 gram H_2O.

	Calculated for $C_{10}H_{22}$.	Found. I.	II.
C	84.51	84.36	84.47
H	15.49	15.38	15.92

Two determinations of the specific gravity at 20° of this oil in different preparations gave 0.7519 and 0.7513.

In a still more extended purification, some of the crude distillate was agitated thoroughly with the mixture of nitric and sulphuric acids, allowed to stand several hours with the acids, and, after washing, heated for some time with tin and hydrochloric acid. The washed and dried oil was then warmed with fuming sulphuric acid, washed, dried, and distilled. It then gave 0.7482 as its specific gravity at 20°, more nearly approaching the specific gravity of the Pennsylvania decane 173°, 0.7467, and analysis indicated that the remaining oil had the composition of the general formula C_nH_{2n+2} : —

0.1449 gram of the oil gave 0.4494 gram CO_2, and 0.2051 gram H_2O.

	Calculated for $C_{10}H_{22}$.	Found.
C	84.51	84.57
H	15.49	15.73

Another quantity of the crude distillate was heated on the steam bath during several hours with fuming sulphuric acid, occasionally shaking the acid with the oil, boiled with sodium, distilled, and dried for analysis: —

0.1519 gram of the oil gave 0.4715 gram CO_2, and 0.2085 gram H_2O.

C	84.67
H	15.26

The specific gravity of this product was the same as before, 0.7514. In a determination of the molecular weight of the hydrocarbon purified by the mixture of nitric and sulphuric acids, tin and hydrochloric acid, fuming sulphuric acid and sodium, Mr. Hudson obtained 142; required for $C_{10}H_{22}$, 142. The fuming sulphuric acid solution separated from the oil was neutralized with baric carbonate filtered and evaporated nearly to dryness. On cooling, a barium salt separated in needles, which were very sparingly soluble in cold water. The air-dried salt was anhydrous, and it gave, by ignition with sulphuric acid, 25.46 per cent of barium. Hexahydrocymol requires 23.8 per cent of barium, and iso-cymol 24.3. The first hydrocarbon boils at 171°–172°, m-cymol at 174°–176°, p-cymol at 172°–173°, and pseudo-cymol at 169°. By fuming sulphuric acid at least the iso-cymol if present in petroleum should be extracted, and it is probable that this barium salt was an impure compound of cymolsulphonic acid. That the decane boiling at 174° is the principal constituent of Ohio petroleum at this point, and that it contains a considerable proportion of aromatic hydrocarbons, has received ample proof. As to the precise form of the aromatic hydrocarbons, the qnantity of material it has been expedient to manipulate in purifying the decane was not sufficient to demonstrate. It would evidently be impossible to separate these bodies from decane in any course of distillation, and it would require a large quantity of the crude distillate, although not so thoroughly distilled as the one prepared in this examination.

In still further evidence as to the formula of this hydrocarbon, the chlorine derivatives were prepared by the action of chlorine on a portion purified with the mixture of nitric and sulphuric acids and sodium. 83 grams of the hydrocarbon was allowed to absorb 30 grams of chlorine, the theoretical quantity for the mono derivative being 20 grams. As an illustration of the readiness with which substitution

takes place, in this experiment the stream of chlorine happened to be exceptionally vigorous, but it was completely absorbed from the beginning to the extent of 5 grams during the first ten minutes. Hydrochloric acid escaped from the oil with brisk effervescence, although the chlorine was delivered at some distance above the surface of the oil. This rapid substitution at low temperatures is quite unlike the substitution of chlorine in dekanaphtene observed by Markownikoff and Oglobine, as shown by the following statement: * "Lorsqu'on fait agir du chlore sec sur les vapeurs du décanaphtène en ébullition et sous l'influence de l'insolation directe, la réaction se fait lentement avec dégagement d'acide chlorhydrique et demande un très grand excès de chlore en comparaison de ce qu'il en faut d'après le calcul théorique." Yet in the residue of the hydrocarbon not acted on by chlorine, Markownikoff and Oglobine found a somewhat lower percentage of carbon and a higher percentage of hydrogen, from which, together with a slightly lower specific gravity, 0.792, than decanaphtene, 0.795, they infer that "ces chiffres semblent indiquer la présence d'une quantité notable d'un hydrocarbure saturé." In accordance with my observations on all the hydrocarbons from Pennsylvania, Ohio, and Canadian oil which I have chlorinated, these bodies should be saturated long before the naphtenes, especially if the latter substitute chlorine slowly at a boiling temperature.

In fractioning *in vacuo* under 80 mm. the chlorinated oil, after several distillations about 8 c.c. collected at 134°–136°, with a small proportion of unaffected hydrocarbon which came over at a lower temperature. Analyses of this product gave numbers corresponding to the composition of chlordecane: —

I. 0.2773 gram of the oil gave 0.6977 gram CO_2, and 0.2886 gram H_2O.

II. 0.1623 gram of the oil gave 0.4085 gram CO_2, and 0.1679 gram H_2O.

III. 0.2117 gram of the oil gave 0.1707 gram AgCl.

	Calculated for $C_{10}H_{21}Cl$.	Found. I.	II.	III.
C	68.00	68.60	68.64	
H	11.90	11.56	11.50	
Cl	20.11			19.93

A determination of the specific gravity of this chlordecane at 20° gave 0.8895. Under atmospheric pressure, it distilled with some decomposi-

* Ann. Chim. Phys., (6.), II. 453.

tion at 205°–210°. Its molecular weight, determined by the Beckmann method, was found by Mr. Hudson to be 174; required for the formula $C_{10}H_{21}Cl$, 176.5.

In continuing the fractional distillation *in vacuo* of the chlorine product from 173° Ohio decane, a small quantity, 3 c.c., collected at 170°–180°, 80 mm., which distilled under atmospheric pressure at 240°–243°. On account of decomposition, this portion was fractioned only five times, but it gave on analysis a percentage of chlorine corresponding to dichlordecane: —

I. 0.2690 gram of the oil gave 0.5549 gram CO_2, and 0.2191 gram H_2O.

II. 0.2753 gram of the oil gave 0.5746 gram CO_2, and 0.2111 gram H_2O.

III. 0.3147 gram of the oil gave 0.4256 gram AgCl.

	Calculated for $C_{10}H_{20}Cl_2$.	Found. I.	II.	III.
C	56.87	56.24	56.94	
H	9.48	9.04	8.51	
Cl	33.65			33.46

A determination of the specific gravity of this dichlordecane at 20° gave 1.0300, which may not be strictly correct on account of the small quantity of the material.

In determining the boiling point of this decane, 50 c.c. of the oil, purified as thoroughly as possible, distilled at 173°.6–174°.6, mostly below 174°, under a tension of 760 mm. and with the mercury column all within the vapor.

The boiling point of normal decane was given by Krafft * as 173° at 760 mm., but 0.7304, its specific gravity at 20°, is sensibly lower than it has been possible to reduce the decane from petroleum. Whether this be due to the presence of a small amount of decanaphtene, which appears to be nearly inert toward the methods of purification that have been applied to these petroleum hydrocarbons, can only be determined in more extended experiments. In view of the ease in chlorination of the hydrocarbons C_nH_{2n+2}, and the difficulty in chlorinating the naphtenes according to the experience of Markownikoff and Oglobine, perhaps fractional chlorination should permit of the removal of decane, and the naphtene would reveal its presence by analysis. As already

* Ber. der deutsch. chem. Gesellsch., XV. 1695.

shown in the case of Pennsylvania dodecane, page 141, the portion remaining after incomplete chlorination is the purified hydrocarbon $C_{12}H_{26}$.

HENDECANE, $C_{11}H_{24}$, 195°–196°.

Above 173° (760 mm.), fractions collected irregularly and in small amounts to 188°. There was no indication of an accumulation in the vicinity of 180°, but after precipitation of the sulphur compounds with $HgCl_2$ considerable quantities collected at 188°–192° (730 mm.), which for the most part came together at 189°–191°. An analysis of the crude distillate gave the following percentages of carbon and hydrogen: —

0.1444 gram of the oil gave 0.2536 gram CO_2, and 0.1888 gram H_2O.

	Required for C_nH_{2n}	
C	85.71	85.67
H	14.29	14.53

A specific gravity determination at 20° gave 0.7789, and a determination of its vapor density by the Hofmann method the following value: —

0.1286 gram of the oil gave 67 c.c. of vapor at 182°, and under 357.5 mm.

Calculated for $C_{11}H_{22}$.	Found.
5.33	5.26

As in the corresponding crude Pennsylvania distillate, the percentage composition of this hendecane based on the above analysis supports the formula C_nH_{2n}, and it is nearly the same as the specific gravity found by Warren, which gave the formula C_nH_{2n}; it is even closer to the value 0.7780, found by Pelouze and Cahours in their distillate from Pennsylvania, or rather from American petroleum. Allusion is made in their papers to distillates prepared from Canadian petroleum, as well as from Pennsylvania petroleum, and their high specific gravity, much higher than Pennsylvania distillates yield, would seem to indicate that they had in hand Canadian distillates. Another portion of the crude distillate 189°–190° was agitated with a mixture of nitric and sulphuric acids, and allowed to stand some time after the heat of the first reaction had moderated. A heavy nitro compound separated, which crystallized on standing. The reaction was far more energetic than in the same distillate from Pennsylvania petroleum, probably on account of a larger proportion of aromatic hydrocarbons. A heavy nitro compound immediately separated as an oil, which crystallized on standing. It was purified by crystallization from

alcohol, in which it is very sparingly soluble, and gave as its melting point 158°–160°, which was not changed by several crystallizations. There are several aromatic hydrocarbons whose boiling points are in this vicinity, but only one forms a nitro derivative with this melting point, isodurol, whose trinitro derivative melts at 156°. It would be interesting to examine these nitro products more fully, but for want of time and material nothing further was done with them.

The specific gravity of the oil was very sensibly diminished by the action of the acid mixture. The first determination gave 0.7688, which was not diminished by further treatment, although this value is somewhat higher than the specific gravity of the Pennsylvania distillate, 0.7581. In determining the boiling point of this product, 50 c.c. distilled entirely at 195°–196°, mostly at 196°, under a tension of 760 mm. After purification of a portion of the crude distillate with fuming sulphuric acid, different preparations of the washed and dried oil gave in the hands of different analysts the following percentages of carbon and hydrogen: —

I. 0.1508 gram of the oil gave 0.4683 gram CO_2, and 0.2055 gram H_2O.

II. 0.1520 gram of the oil gave 0.4715 gram CO_2, and 0.2109 gram H_2O.

III. 0.1523 gram of the oil gave 0.4733 gram CO_2, and 0.2180 gram H_2O.

	Calculated for $C_{11}H_{22}$.	Found. I.	II.	III.
C	84.63	84.70	84.61	84.75
H	15.38	15.15	15.42	15.90

The specific gravity of the purified oil was found to be 0.7737 at 20°, and the vapor density as follows: —

0.1421 gram of the oil gave 68.6 c.c. of vapor at 182° under 373.8 mm.

Calculated for $C_{11}H_{22}$.	Found.
5.33	5.43

A determination of its molecular weight by Mr. Hudson gave 158; required for the formula $C_{11}H_{24}$, 156.

In attempting to form the chlorine derivatives of this hydrocarbon, 16 grams of the fraction 196°, Ohio petroleum, the small amount that remained for this experiment, was treated with chlorine until it gained in weight 4.5 grams. After the chlorine product was fractioned four times

it collected in very small quantity at 150°–155°. Analysis gave results corresponding to the formula $C_{11}H_{23}Cl$.

I. 0.2042 gram of the substance gave 0.1548 gram AgCl.
II. 0.1938 gram of the oil gave 0.4765 gram CO_2, and 0.2071 gram H_2O.

	Calculated for $C_{11}H_{23}Cl$.	Found. I.	Found. II.
C	69.29		69.74
H	12.07		11.88
Cl	18.63	18.71	

Evidently the chlorination had proceeded so far that the monochlorhendecane could not be separated completely from the dichlor derivative, as shown by the high boiling point, and the large percentage of carbon.

The small amount of the dichlor derivative was not sufficient when purified to give satisfactory analytical data in support of its composition.

Dodecane, $C_{12}H_{26}$, 214°.

Above 193° the distillation was continued longer *in vacuo*. At the end of the eighteenth, between 120° and 130°, 1200 grams collected in single degree fractions, for the most part at 122°–124° and 128°–130°.

The latter distilled under atmospheric pressure at 212°–214°, and was therefore selected for the study of the hydrocarbon which according to the corresponding distillate in Pennsylvania oil should contain $C_{12}H_{26}$. The crude distillate gave the following percentages of carbon and hydrogen: —

	Calculated for $C_{12}H_{24}$.	Found
C	85.51	85.76
H	14.49	14.55

The specific gravity of this distillate at 20° was 0.7877. 25 grams of the crude distillate was heated with fuming sulphuric acid to 50°, and kept warm on the steam bath during several hours. Very little sulphurous acid was set free, although the acid became thick and dark. The loss in weight of the oil was 4.5 grams, or 18 per cent. The remaining oil was washed with sodic hydrate and water, and dried over sodium for analysis.

0.1500 gram of the oil gave 0.4650 gram CO_2, and 0.2088 gram H_2O.

	Calculated for $C_{12}H_{26}$.	Found.
C	84.70	84.54
H	15.30	15.47

A determination of its specific gravity at 20° gave 0.7867, with scarcely any change by the action of the fuming acid. Another portion of the crude distillate was shaken with a mixture of nitric and sulphuric acids. The great heat of the reaction was controlled by cooling, and the heavy nitro product allowed to separate by standing. The principal reaction was soon over, the nitro compound separating in needles on standing.

In hot alcohol the nitro derivative was readily soluble, but quite insoluble in cold alcohol. It melted at 165°, and was probably a derivative, or perhaps a mixture of derivatives, of the aromatic hydrocarbons with boiling points in this vicinity, such as isohexylbenzol, or isoamylbenzol, boiling points 212°–214°, and quite probably contained in petroleum. After treatment with the acid mixture, the oil was boiled with tin and hydrochloric acid, washed, and boiled with sodium, then distilled. Its boiling point was not appreciably changed, but the specific gravity was reduced to 0.7727, a value practically the same as that of the Pennsylvania dodecane. A determination of its molecular weight by the Beckmann method gave 172; required for $C_{12}H_{26}$, 170.

In forming the chlorine derivates of this hydrocarbon, 35 grams absorbed 8.5 grams of chlorine, and the product was fractioned under 80 mm. After the tenth distillation, about 15 c.c. collected at 150°–160°. In this instance, as in one or two others, the distillate taken for chlorination was not purified, and in the distillation the vapors affected the eyes seriously, doubtless on account of substitution in the side chain in the aromatic hydrocarbons contained in the crude distillate. Either on account of decomposition, or want of sufficient material for complete separation, it was not possible to purify this product sufficiently to give satisfactory numbers on analysis, although the results show the formation of a mono- and a dichlor dodecane. The percentage of chlorine in the distillate 150°–160° came two per cent too low for monochlor dodecane, and no combustion was made. In a higher distillate collected at 190°–200° the following numbers were obtained: —

I. 0.2224 gram of the oil gave 0.2607 gram AgCl.
II. 0.1952 gram of the oil gave 0.4411 gram CO_2, and 0.1816 gram H_2O.

	Calculated for $C_{12}H_{24}Cl_2$.	Found I.	Found II.
C	60.26		61.63
H	10.04		10.33
Cl	29.71	28.99	

While, therefore, the formula of dodecane in Ohio petroleum is not supported by such reliable data as those of the lower constituents, the presence of this hydrocarbon is established, I think, beyond question.

The principal constituents of Ohio petroleum have been shown to be identical with those of Pennsylvania petroleum. The higher specific gravity and peculiar qualities of the Ohio distillates depend on the larger proportions of aromatic hydrocarbons, and perhaps of other heavy constituents.

Constituents of Canadian Petroleum from the Corniferous Limestone.

In continuing the study of the higher portions of Canadian petroleum, the vacuum distillates 150°–300° * were carried through fifteen additional distillations under 50 mm. As the separations proceeded, the fractions fell 50° or more in boiling points, large portions collecting below 220°, the point where the separations could be continued without serious decomposition under atmospheric pressure. In single degree fractions after the fifth, distillation was continued until the operation had been repeated in all twenty-nine times. As in the other oils, the distillates collected mainly at 159°–161°, 168°–170°, 188°–191°, and 208°–210° (730 mm.). There is even greater necessity in the Canadian than in the Ohio oil that the earlier distillations be carried on *in vacuo*, on account of the greater quantity of sulphur compounds, but more especially, as will be seen in another paper, on account of the greater proportion of unsaturated hydrocarbons and the smaller proportions of the members in question that distill between 160° and 216°. It is, therefore, otherwise impossible to obtain a large proportion of these higher constituents uncontaminated by impurities due to cracking. But the vacuum distillates are free from the intensely disagreeable odors due to cracking, which are far more pronounced than any to be obtained from Ohio oil. Nevertheless, the natural odor of these compounds, however carefully they have been protected from decomposition before purification, is more pungent than those from Ohio oil. Colorless when first distilled, all these distillates become colored on standing, probably on account of polymerism of the unsaturated hydrocarbons alluded to above, and of other unstable bodies resembling the terpenes, which we have good evidence are contained in petroleum. That this is unquestionably the cause of the coloration we have abundant evidence in the polymeri-

* Proc. Amer. Acad., XXXI. 52.

zation and the formation of heavier oils in these unsaturated bodies after they have been separated and allowed to stand as long as two years. As further evidence that these unstable bodies are the cause of the color, after they have been removed, the purified oils remain colorless permanently. The higher specific gravity observed in the first vacuum distillate from Canadian crude petroleum is still retained in the single degree fractions, however long the fractional distillation is continued. But although these portions are heavier than the distillates from Pennsylvania and Ohio oils, they are so much lighter than the naphtenes that the latter bodies cannot be present in any considerable quantity. In general the ready and abundant formation of nitro derivatives and sulphonic acids is sufficient evidence that the greater specific gravity is due, for the most part at least, to the aromatic constituents. It is quite probable that naphtenes are present in small amounts, and that they are accountable, as has been suggested, for the extreme difficulty in removing the last traces of the less hydrogenized constituents by fuming sulphuric acid, even after vigorous treatment several times repeated. In some instances, nitric and sulphuric acids have given nitro products that have required very long and vigorous boiling with tin and hydrochloric acid for complete reduction, or an equivalent treatment with sodium. Occasionally the reduction with tin and acid has caused the separation of a heavy red oil insoluble in the acid, consequently not an amine.

Decane, $C_{10}H_{22}$, 163°–164°.

The composition of the principal distillates from Canadian petroleum below 150° was found to be represented by the series C_nH_{2n+2}. Above this point the distillates were small to 158°, but between this point and 162° larger amounts collected and remained persistently at 159°–160° (730 mm.). After treatment with fuming sulphuric acid, a portion of this distillate was still further fractioned until 75 grams distilled at 163°–164° under 760 mm., and with the mercury column all in the vapor. In the crude distillate before treatment with the acid, carbon and hydrogen were determined, with no other purification than drying over sodium. No less efficient means of desiccation removes the water sufficiently for analysis. But since a reddish flocculent precipitate separates when any of these distillates stand with sodium, evidently the percentages of carbon and hydrogen in the crude distillates cannot be accurately expressed by the results of combustion. The precipitation is doubtless caused in part by sulphur compounds which are not wholly removed by alcoholic mercuric chloride, although it is observed when the quantity of sulphur is very small.

0.1610 gram of the oil gave 0.5057 gram CO_2, and 0.1989 gram H_2O.

C	85.67
H	13.72

Before treatment with the acid, a determination of specific gravity at 20° gave 0.7785. After purification with the acid the specific gravity was diminished to 0.7572, nearly the same value as that found in the corresponding fraction of Ohio oil. The penetrating odor of the crude distillate, resembling that of the aromatic hydrocarbons, disappeared entirely after treatment with the fuming acid, and the purified oil gave only the faint characteristic odor of the petroleum hydrocarbons C_nH_{2n+2}. The acid was blackened and gave off much sulphurous acid. 30 grams gave by this treatment 23.4 grams of the purified oil with a loss of 22 per cent. It is interesting to note the higher specific gravity of the unpurified distillate 163°–164° in all these oils — Pennsylvania, Canadian, and Ohio — than that of the higher distillate, 174°. This clearly indicates a larger percentage of mesitylene and perhaps of decanaphtene. The difficulty in removing entirely the heavier body would seem to indicate a trace of the latter.

After the last distillation, the oil was again treated with the fuming acid and dried over sodium for analysis: —

0.1723 gram of the oil gave 0.5358 gram CO_2, and 0.2304 gram H_2O.

	Calculated for		
	$C_{10}H_{20}$	$C_{10}H_{22}$	Found.
C	85.71	84.51	84.82
H	14.29	15.49	14.85

The oil was again subjected to the action of the acid and analyzed: —

0.1561 gram of the oil gave 0.4847 gram CO_2, and 0.2127 gram H_2O.

C	84.67
H	15.14

The slight change in the percentages of carbon and hydrogen evidently shows the presence of a heavy body that is but slowly affected by the acid. This impurity cannot be mesitylene, since this hydrocarbon dissolves readily in the fuming acid. Another portion of the crude distillate was next vigorously agitated with a mixture of nitric and sulphuric acids, allowing the temperature to rise spontaneously nearly to 100°. As soon as the principal action ceased, the mixture cooled and an oily nitro body

separated, more remaining in solution. After several crystallizations from alcohol, in which it is quite insoluble, the nitro derivative melted at 225°, near the melting point of trinitromesitylene. The hydrocarbon oil was separated from the acid and boiled several hours with tin and hydrochloric acid, which caused the yellow color to be absorbed by the acid solution, and a small amount of a heavy oil separated, insoluble in the acid, evidently a product of the vigorous reduction. The crude distillate lost 20 per cent in weight by this purification. The oil remaining after the reduction, when shaken with fuming sulphuric acid, washed, and dried, gave only the characteristic odor of the petroleum hydrocarbons. Upon analysis it gave the following results: —

0.1455 gram of the oil gave 0.4517 gram CO_2, and 0.1980 gram H_2O.

	Calculated for $C_{10}H_{22}$	Found.
C	84.51	84.67
H	15.49	15.12

While these results point clearly to the composition C_nH_{2n+2} for the principal hydrocarbon with this boiling point, they also suggest, as has already been mentioned, a constituent of Canadian oil so inert toward reagents that it cannot be removed by ordinary means. No doubt the difficulty is increased by the great dilution of this impurity in the larger body of the decane. In its behavior toward reagents, dekanaphtene is suggested. Whatever may be the composition of this body, it is doubtless present in largest quantity in Canadian petroleum, a smaller amount in Ohio oil, and a still smaller proportion in Pennsylvania oil. But even in the Canadian oil, the proportion is evidently very small.

The formula of the principal constituent at 163° found still further support in a determination of its molecular weight by the method of Beckmann, in which Mr. Hudson obtained 142; the formula $C_{10}H_{22}$ requires 142.

The purified distillate 160°–161°, Canadian petroleum, behaved toward chlorine precisely like the corresponding distillates from Ohio and Pennsylvania oils. 17 grams absorbed 4 grams chlorine, and was then fractioned *in vacuo*. About 1 c.c. was obtained after five distillations at 200°–204° atmospheric pressure, without decomposition, and it gave by analysis the composition required for $C_{10}H_{21}Cl$: —

I. 0.1922 gram of the substance gave 0.1536 gram AgCl.

II. 0.1873 gram of the substance gave 0.4710 gram CO_2, and 0.207 gram H_2O.

	Calculated for $C_{10}H_{21}Cl$.	Found. I.	II.
C	68.00		68.58
H	11.90		12.30
Cl	20.11	19.77	

The quantity of this monochlor decane was too limited to permit of further determinations, as were also the higher portions for the separation of a dichlor derivative sufficiently pure for analysis.

Having at hand a small quantity of the distillate 162°, Berea Grit petroleum, it seemed of interest to ascertain whether it would form a chlorine derivative similar or identical with those of the oils now under examination. 30 grams of the oil absorbed 8 grams of chlorine in forty-five minutes, and when the product was fractioned it gave a small quantity at 120°–130° with the composition required for $C_{10}H_{21}Cl$: —

I. 0.1931 gram of the substance gave 0.1564 gram AgCl.

II. 0.1821 gram of the substance gave 0.4486 gram CO_2, and 0.1871 gram H_2O.

	Calculated for $C_{10}H_{21}Cl$.	Found I.	II.
C	68.00		67.19
H	11.90		11.41
Cl	20.11	20.04	

The formation of this chlordecane confirms the results published in a former paper * of this series, showing a hydrocarbon $C_{10}H_{22}$ in Berea Grit petroleum with the boiling point 162°.

Decane, 173°–174°.

Above 163° (730 mm.) the absence of single bodies was indicated by the small amounts of distillates to 168°, where the single degree fractions began to increase in quantity. Between this point and 173° nearly 500 grams collected, the greater portion at 169°–171°, which could not be brought closer together without further purification. After drying over sodium, analysis of this distillate gave the following percentages of carbon and hydrogen : —

0.1640 gram of the oil gave 0.5151 gram CO_2, and 2083 gram H_2O.

C	85.66
H	14.11

* Amer. Chem. Journ., XVIII. 1.

A determination of the specific gravity of this distillate at 20° gave 0.7770, a value somewhat higher than the specific gravity of the corresponding Ohio distillate. For the removal of the aromatic hydrocarbons to determine the boiling point of the principal constituent, all the fractions 168°–173° were agitated and warmed with fuming sulphuric acid, washed, dried, and the distillation continued until after a few repetitions the fractions came together at 169°–170° (730 mm.), or under 760 mm., and with the mercury column all in the vapor at 173°–174°. By this treatment the specific gravity was reduced to 0.7614, and the percentages of carbon and hydrogen changed in a proportionate degree: —

I. 0.1545 gram of the oil gave 0.4810 gram CO_2, and 0.2091 gram H_2O.

II. 0.1446 gram of the oil gave 0.4485 gram CO_2, and 0.1946 gram H_2O.

III. 0.1678 gram of the oil gave 0.5204 gram CO_2, and 0.2246 gram H_2O.

	Calculated for		Found.		
	$C_{10}H_{20}$	$C_{10}H_{22}$.	I.	II.	III.
C	85.71	84.51	84.90	84.59	84.57
H	14.29	15.49	15.04	14.96	14.89

Although these results indicate the removal of a large portion of the aromatic hydrocarbon, and analyses II. and III. were made of different specimens with the action of the acid continued several hours, it is evident that the less hydrogenized body was not even then entirely removed. In further confirmation of the presence still of this constituent, one of the oils treated with the fuming acid was shaken with a mixture of nitric and sulphuric acids. The solution became warm and an oily nitro product separated above the acid. Since Markownikoff preferred purification of the Russian oil with sulphuric acid to avoid the formation of objectionable nitro products, it was inferred that this acid should remove completely the aromatic bodies. But in our experience with American oils, complete purification cannot be reached with the fuming acid alone. At first we relied on decomposition of the nitro product with sodium; but this required long digestions several times repeated, and in Canadian distillates the residual hydrocarbon which contained the nitrogen could not always be entirely removed, as shown by analysis of a portion of crude distillate purified in this manner: —

I. 0.1656 gram of the oil gave 0.5156 gram CO_2, and 0.2241 gram H_2O.

II. 0.1736 gram of the oil gave 0.5419 gram CO_2, and 0.2345 gram H_2O.

	Calculated for $C_{10}H_{22}$.	Found. I.	Found. II.
C	84.51	84.90	85.13
H	15.49	15.04	15.01

The specific gravity of this distillate was found to be 0.7618, the same as that purified by fuming sulphuric acid. Another portion of the same crude distillate was treated with the mixture of concentrated nitric and sulphuric acids. The great heat developed was controlled by cooling, and finally the heavy nitro product collected above the acid. 25 grams of the crude distillate lost 9 grams in the formation of the nitro product, equivalent to 36 per cent. In another experiment 25 grams of the crude distillate treated with fuming sulphuric acid lost 6 grams, or 24 per cent. The oil remaining after the first experiment was again treated with the mixture of acids, which caused further separation of the nitro product. For the removal of the nitro compound, the oil was boiled during several hours with tin and hydrochloric acid. The reduction was very slow and a red oil separated, leaving the upper layer colorless. The latter was then agitated with concentrated sulphuric acid, washed, dried, and analyzed: —

0.1449 gram of the oil gave 0.4494 gram CO_2, and 0.2051 gram H_2O.

	Calculated for $C_{10}H_{22}$.	Found.
C	84.51	84.57
H	15.49	15.73

The oily nitro derivative of the aromatic hydrocarbon deposited crystals on standing, which after recrystallization from hot alcohol, in which it was very sparingly soluble, melted at 169°. The quantity obtained was insufficient for analysis.

The specific gravity of the oil purified as described above was 0.7601, and, as shown by the vigorous means of purification employed, it cannot easily be reduced, although it is materially larger than the specific gravity of the decane 173° separated from Ohio oil, 0.7513, and of the decane from Pennsylvania oil, 0.7467. But the analyses show that the principal constituent is a hydrocarbon of the series C_nH_{2n+2}. The molecular weight of this hydrocarbon, determined by the Beckmann method, gave Mr. Hudson 144; required by the formula $C_{10}H_{22}$, 142.

In forming the chlorine derivative of this fraction, 35 grams was exposed to the action of chlorine until it had increased in weight 12 grams. After ten distillations *in vacuo*, 5 c.c. were collected at 135°–138°, which upon analysis gave values required for $C_{10}H_{21}Cl$: —

I. 0.1950 of the oil gave 0.4835 gram CO_2, and 0.2143 gram H_2O.
II. 0.2083 gram of the oil gave 0.1672 gram AgCl.

	Calculated for $C_{10}H_{21}Cl$.	Found. I.	Found. II.
C	68.00	67.69	
H	11.90	12.21	
Cl	20.11		19.86

The crude distillate having been used in the preparation of the chlorine derivatives, the action on the eyes during distillation was severe, doubtless due to substitution in the side chain of the aromatic hydrocarbons contained in the unpurified oil.

In distilling the higher fractions, 5 c.c. collected at 170°–180° that distilled under atmospheric pressure at 205°–210°. It was shown by analysis to have the composition required for $C_{10}H_{20}Cl_2$: —

I. 0.2405 gram of the substance gave 0.3214 gram AgCl.
II. 0.2057 gram of the substance gave 0.4352 gram CO_2, and 0.1772 gram H_2O.

	Calculated for $C_{10}H_{20}Cl_2$.	Found. I.	Found. II.
C	56.87		57.69
H	9.48		9.57
Cl	33.65	33.02	

The specific gravity of this dichlordecane was found to be 1.0484. A determination of its molecular weight by the Beckmann method gave 207; the formula $C_{10}H_{20}Cl_2$ requires 211.

HYDROCARBON, $C_{11}H_{22}$.

Above 173°, the absence of a definite product was shown by the small amount of the distillates to 188°. Especial attention was given to the fractions in the vicinity of 180° with reference to the possibility of a naphtene, since the naphtene $C_{12}H_{24}$ boiling at 180°–185° was separated by Markownikoff from Russian oil, and Pelouze and Cahours found a hydrocarbon C_nH_{2n+2} boiling at 180°–182° in American (Canadian?) petroleum. But the very small amounts collected within these limits

precluded the presence of either of these bodies in any appreciable quantities in Canadian petroleum. The portions distilling between 188° and 200° were gradually brought together at 189°–191°. A portion of the crude distillate was treated with fuming sulphuric acid and still further fractioned until for the most part it came together at 196°–197° under 760 mm., and with the mercury column all in the vapor. In drying the crude distillate with sodium for analysis the usual reddish flocculent precipitate separated, which doubtless changed somewhat the composition of the oil: —

0.1565 gram of the oil gave 0.4921 gram CO_2, and 0.2041 gram H_2O.

C	85.74
H	14.49

This oil gave 0.7889 as its specific gravity at 20°, and after treatment with ordinary sulphuric acid 0.7856, the slight difference indicating that this acid has very little action in the cold on this distillate, although the acid was considerably blackened, and sulphurous acid was observed. Another portion of the crude distillate with fuming sulphuric acid developed no heat, and when warmed on the steam bath the acid was only slightly colored. After this treatment the specific gravity was 0.7832, nearly the same as before. A third portion of the original distillate was agitated with a mixture of concentrated nitric and sulphuric acids. Very little heat was developed, and the mixture was then warmed on the steam bath. A small amount of nitro product separated as an oil, which crystallized on standing. After crystallization from alcohol, the nitro derivative melted at 150°–154°, near the melting point of dinitroisodurol, 156°. After heating a long time with sodium, until there was no further action, the specific gravity was found to be 0.7785. The purified oil was submitted again to the same treatment, when its specific gravity was 0.7758. Still another treatment of the same oil with the mixture of acids and boiling with sodium, also boiling with tin and hydrochloric acid, and agitating with fuming sulphuric acid, reduced the specific gravity only to 0.7729. Analysis I. was made of the oil after the first treatment with the mixture of acids and sodium, and analysis II. of the oil after the third treatment: —

I. 0.1562 gram of the oil gave 0.4901 gram CO_2, and 0.2051 gram H_2O.

II. 0.1628 gram of the oil gave 0.5093 gram CO_2, and 0.2095 gram H_2O.

	Calculated for		Found.	
	$C_{11}H_{24}$.	$C_{11}H_{22}$.	I.	II.
C	84.70	85.71	85.57	85.33
H	15.30	14.29	14.59	14.30

A determination of the molecular weight by the method of Beckmann gave 154; the formula $C_{11}H_{22}$ requires 154.

These results indicate the series C_nH_{2n}, and that the series C_nH_{2n+2} has ceased to represent the principal composition of Canadian petroleum at the boiling point 196°. But with reference to the series of hydrocarbons that are now recognized as constituting the main body of petroleum, it is not easy to classify this hydrocarbon. It is certainly not an unsaturated member of the ethylene series because it lacks additive power for the halogens, fuming sulphuric acid, etc. Its specific gravity is much less than that of the naphtene that Markownikoff and Oglobine separated at 196°–197° from the Russian oil, 0.8010 at 20°. But it is interesting to observe that the specific gravity of this hydrocarbon is practically the same as Pelouze and Cahours found in the hydrocarbon separated by them at 196°–200° from American petroleum, and which yielded them analytical values, as has already been explained, page 134, corresponding closely to the formula $C_{12}H_{26}$. Since the specific gravity of Pelouze and Cahours is so much larger than that of the crude distillate from Pennsylvania petroleum, 0.7673, it is difficult to escape the conviction that their distillates were prepared from Canadian petroleum, especially since they allude to an examination of oil from Canada, although the source of the particular oil from which were separated the individual hydrocarbons which they described is not evident from their statements.

In studying the constituents of Pennsylvania oil, it has already been shown that chlorine acts less readily on the principal hydrocarbons than on other constituents. Since this difference on the action of chlorine seemed to afford a means of ascertaining whether Canadian distillates contain any of the series C_nH_{2n+2}, a small quantity, 16 grams, of the distillate 189°–190° purified with fuming sulphuric acid remaining after the examination already described, was exposed to the action of chlorine until three grams was absorbed, and the product was fractioned *in vacuo* until a small portion, six grams, distilled at 189°–190° atmospheric pressure. This fraction was boiled with sodium to remove, so far as possible, any chlorine derivative remaining, shaken with sulphuric acid, and again distilled. There was finally obtained about three grams that gave percentages of carbon and hydrogen agreeing fairly well for $C_{11}H_{24}$.

The low values are due to a small amount of chlorine that was not entirely removed even by the treatment with sodium: —

0.1558 gram of the oil gave 0.4803 gram CO_2, and 0.2115 gram H_2O.

	Calculated for $C_{11}H_{24}$.	Found.
C	84.70	84.09
H	15.30	15.09

In the formation of chlorine derivatives from the purified fraction 196°, Canadian petroleum, 25 grams absorbed 7 grams chlorine. After five distillations *in vacuo*, 3 c.c. collected at 145°–150°, which distilled at 220°–228° atmospheric pressure, and by analysis gave values required for $C_{11}H_{21}Cl$: —

I. 0.2378 gram of the substance gave 0.1747 gram AgCl.

II. 0.2005 gram of the oil gave 0.5105 gram CO_2, and 0.2097 gram H_2O.

	Calculated for $C_{11}H_{23}Cl$.	Found. I.	Found. II.
C	70.03		69.44
H	11.14		11.62
Cl	18.83	18.18	

A determination of the specific gravity of the monochloride at 20° gave 0.8882. With the small quantity of the higher distillates, it was not possible to separate a dichlor derivative in any degree of purity.

The small amount of the monochloride evidently precluded the possibility of ascertaining with any precision the true boiling point, and the analysis is chiefly of value in determining the number of carbon atoms in the molecule. The number of carbon atoms received still further confirmation in a determination of the molecular weight by the Beckman method, which gave 187; the formula $C_{11}H_{21}Cl$ requires 188.5.

HYDROCARBON, $C_{12}H_{24}$.

Above 195° (730 mm.) the distillates were small in quantity to 208°, but between 208° and 212° about 300 grams collected, for the most part at 208°–210°. The specific gravity of the crude distillate was found to be 0.7947, and analysis gave the following percentages of carbon and hydrogen: —

0.1554 gram of the oil gave 0.4878 gram CO_2, and 0.1982 gram H_2O.

	Required for C_nH_{2n}.	Found.
C	85.71	85.57
H	14.29	14.18

In order to collect this distillate more closely, a portion of the crude oil was treated with fuming sulphuric acid, washed, dried, and the distillation continued. 37 grams of the oil gave 27 grams after purification. After several distillations it collected at 212°–214° under 745 mm., and with the mercury all within the vapor. Two determinations of specific gravity at 20° gave (I.) 0.7851, and (II.) 0.7857. The carbon and hydrogen were also determined: —

0.1586 gram of the oil gave 0.4960 gram CO_2, and 0.2105 gram H_2O.

	Calculated for $C_{12}H_{24}$.	Found. I.
C	85.71	85.27
H	14.29	14.74

These values point to the composition C_nH_{2n} for this constituent of the Canadian oil. In further evidence as to the correctness of this result, another portion of the crude distillate was shaken with a mixture of concentrated nitric and sulphuric acids, the intense heat at first generated controlled, and after the principal action had ceased the solution was kept warm for some time on the steam bath. An oily nitro product collected above the acid in considerable quantity, but it was not further examined. The hydrocarbon remaining was then agitated with concentrated sulphuric acid, washed with caustic soda, which removed much more of the nitro product from the oil, then with water, and boiled for some time with tin and hydrochloric acid.

The oil remaining was then washed, dried, and warmed during several hours with fuming sulphuric acid, which produced little change, and boiled with sodium. After this purification, analysis still gave values required for a hydrocarbon C_nH_{2n}.

I. 0.1383 gram of the oil gave 0.4332 gram CO_2, and 0.1849 gram H_2O.
II. 0.1406 gram of the oil gave 0.1856 gram H_2O.

	Calculated for $C_{12}H_{24}$.	Found. I.	II.
C	85.71	85.41	Lost.
H	14.29	14.86	14.68

In forming the chlorine derivatives of this hydrocarbon, 26.5 grams of the fraction 214°–216° was allowed to absorb chlorine until the weight had increased 9.5 grams, and the product was fractioned eight times *in vacuo;* 5 c.c. collected at 160°–170°, which gave on analysis the percentage composition required for $C_{12}H_{23}Cl$.

I. 0.2059 gram of the substance gave 0.1515 gram AgCl.

II. 0.2064 gram of the substance gave 0.5357 gram CO_2, and 0.2128 gram H_2O.

	Calculated for $C_{12}H_{23}Cl$.	Found. I.	II.
C	71.06		70.79
H	11.30		11.46
Cl	17.53	18.20	

The specific gravity of this chlorine derivative determined at 20° was found to be 0.8960. The small quantity of distillate collected within higher limits did not permit of the separation of a dichlor derivative in a pure condition. A chlorine determination gave 27.21 ; required for $C_{12}H_{22}Cl_2$, 29.95. It formed a thick viscous oil that could scarcely be distilled even *in vacuo* without decomposition. At a temperature slightly higher than where this product was collected the distillate was largely decomposed.

The series having been determined by these numbers, the number of carbon atoms was demonstrated by the molecular weight, which was found by the Beckmann method to be 172 ; the formula $C_{12}H_{24}$ requires 168.

What has been said as to the probability that Pelouze and Cahours operated on Canadian petroleum receives further support in comparing their results on the hydrocarbon they separated boiling at 216°–218° with those described above, although certain important differences appear between their results and mine.

The specific gravity assigned by them to the hydrocarbon 216°–218° was 0.796 at 20°, which is practically the same as the specific gravity of my crude distillate, 0.7947, given above. But their description of the properties of this distillate are not in accordance with my observations. Referring to the action of reagents on their product, they state : "Le brome, l'acide azotique fumant, l'acide sulfurique fumant, ainsi que le mélange de ces deux acides se comportent à son égard comme avec le composé précédent." And after stating, in the description of the preceding compound, that it is not attacked in the cold by bromine, fuming nitric acid, sulphuric acid at the maximum of concentration with nitric acid, nor by fuming sulphuric acid, they state : "Le mélange des acides azotique et sulfurique agit sur le carbure lorsqu'on maintient ces corps pendant quelque temps en ébullition." That this observation does not represent correctly the behavior of this distillate from Pennsylvania nor Ohio, nor Canadian petroleum, has been clearly shown by experiments described in this paper. It is especially inapplicable to the Canadian distillate,

since this oil with a mixture of ordinary concentrated nitric and sulphuric acids, on shaking, immediately develops sufficient heat to raise the temperature to vigorous ebullition of the acid mixture, and to destroy a large portion of the hydrocarbon. In all these experiments the initial reaction had to be controlled by cooling.

Concerning the number of carbon atoms in the hydrocarbon I have separated at this point, it seems to be well established by the molecular weight, $C_{12}H_{24}$, and by the composition of the monochlor derivative, $C_{12}H_{23}Cl$. Yet in a product with a specific gravity much higher than this purified hydrocarbon, Pelouze and Cahours obtained numbers by analysis, as shown above, page 141, closely supporting the formula $C_{13}H_{26}$, and from the hydrocarbon a chlorine derivative, $C_{13}H_{27}Cl$, also supported by analytical values closely corresponding to the theoretical composition required for this formula.

Summary of Results.

1. Pennsylvania petroleum is composed chiefly between 150° and 220° of decane, boiling point 163°–164°; decane, boiling point 173°–174°, probably normal decane; hendecane, boiling point 196°–197°; and dodecane, boiling point 214°–216°. It contains also in smaller proportions the series of aromatic hydrocarbons boiling within these limits. Allusion has already been made to mesitylene, cumol, pseudocumol, cymol, isocymol, durol, isodurol, and no doubt others could be identified with sufficient quantities of the petroleum distillates.

2. The composition of Ohio Trenton Limestone petroleum within the same limits is represented by the same members of the series C_nH_{2n+2}, and the higher specific gravity of these distillates is caused by a larger proportion of aromatic hydrocarbons.

3. The constituents of Canadian Corniferous limestone petroleum from Petrolia, within these limits of temperature, are the same at 163° and 173°. But the hydrocarbons collecting at 196° and 214° have the composition represented by the series C_nH_{2n}. Probably a better knowledge of these higher distillates will be gained when the true composition of American petroleum above 220° has been ascertained. The proportion of aromatic hydrocarbons is greater in Canadian than in Ohio petroleum. There are indications in all these petroleums that the heavier constituents include other bodies than the aromatic hydrocarbons, which will require for their identification the manipulation of large quantities of distillates.

General Conclusions.

The results described in this paper make it clear that no conclusions can be arrived at concerning the composition of the principal constituents of American petroleum between 151° and 216° without separating from these bodies the various impurities with which they are contaminated in the crude distillates. However far fractional distillation may be carried, it is impossible to effect a separation of those bodies whose boiling points do not differ by more than a few degrees. But fortunately the principal constituents of petroleum are not affected by reagents under conditions which allow the removal of the contaminating bodies. While the statement of Pelouze and Cahours that the portions of American petroleum under consideration are not affected by nitric acid nor by fuming sulphuric acid is not supported by the behavior of distillates used by me in this examination, it is true that the principal constituents are not acted upon by those reagents under conditions that permit of purification. A casual examination of the literature of Pennsylvania petroleum is sufficient to reveal the uncertainty and confusion in statements concerning the composition of the portions with higher boiling points. The principal constituents have more commonly been referred to the series C_nH_{2n+2}, as suggested by Pelouze and Cahours, who included in this series all the petroleum hydrocarbons, even the least volatile oils and paraffine, although on the basis of Warren's investigations allusions have been made to the unsaturated olefine hydrocarbons C_nH_{2n} as constituting the main body of Pennsylvania petroleum above 150°, and the belief has been expressed that the naphtene series C_nH_{2n} should best explain Warren's results. As already stated, above 150° Pelouze and Cahours separated distillates at 162°, 182°, 196°–200°, and 216°–218°, which, with no especial purification, gave analytical data corresponding closely with the theoretical values for the series C_nH_{2n+2}. That there are marked differences in the specific gravity of crude and refined distillates appears in the purification of all distillates described in this paper, and it is no easy task to purify the crude distillates so that they shall yield satisfactory analytical data. As shown in the following table, the specific gravity determinations by Pelouze and Cahours in the products they analyzed are essentially different from those in Pennsylvania distillates herein presented. The percentages of carbon and hydrogen required for the series C_nH_{2n+2} were obtained in fractions whose specific gravity was even higher than our crude distillates, which gave values closely agreeing with the series C_nH_{2n}. This difference in specific gravity can only be explained

by assuming, which is evidently true, that Pelouze and Cahours overlooked the aromatic hydrocarbons. It does not appear in their reference to American petroleum whether they really operated on distillates from Pennsylvania oil; but, on the other hand, their specific gravity determinations are not widely different from those of distillates from Canadian oil to which occasional reference is made in their publications.

PENNSYLVANIA PETROLEUM.

Fraction. C. F. M. Unpurified.	Fraction. C. F. M. Purified.	Fraction. P. & C.	Specific Gravity. C. F. M.	Specific Gravity. P. & C.	Series.
163°–164°			0.7684 (20°)		C_nH_{2n}
	163°–164°		0.7479 (20°)		C_nH_{2n+2}
		162°		0.757 (15°)	C_nH_{2n+2}
196°–197°			0.7673 (20°)		C_nH_{2n}
	196°–197°		0.7581 (20°)		C_nH_{2n+2}
		196°–200°		0.7780	C_nH_{2n+2}
214°–216°			0.7745 (20°)		C_nH_{2n}
	214°–216°		0.7684 (20°)		C_nH_{2n+2}
		216°–218°		0.796	C_nH_{2n+2}

CANADIAN PETROLEUM.

Fraction Unpurified.	Fraction Purified.	C. F. M.
163°–164°		0.7785
	163°–164°	0.7582
196°–197°		0.7889
	196°–197°	0.7729
214°–216°		0.7947
	214°–216°	0.7851

If the results of Pelouze and Cahours were really obtained in distillates from Canadian petroleum, as seems probable, especially since Pennsylvania distillates do not yield such high values, the specific gravity determinations in their lower distillates agree fairly well with mine in the purified Canadian hydrocarbons.

The results of Warren, on the other hand, are consistent in giving numbers that account both in specific gravity and in percentage composition for the complex mixture that crude petroleum distillates are known to be. While Warren made no attempts to purify his distillates, they were obtained in a course of fractional separations far exceeding in efficiency those of other experimenters. It is interesting to observe in the following

table how closely the distillates from Pennsylvania petroleum analyzed by Warren resemble in specific gravity the unpurified distillates described in this paper.

Fraction. Unpurified.	Fraction. Purified.	Specific Gravity. Mabery.	Specific Gravity. Warren.	Series.
163°–164°		0.7674 (20°)		C_nH_{2n}
173°.5		0.7502 (20°)		C_nH_{2n}
	173°.5	0.7445 (20°)		C_nH_{2n+2}
175°			0.7598 (15°)	C_nH_{2n}
196°		0.7673 (20°)		C_nH_{2n}
	196°	0.7581 (20°)		C_nH_{2n+2}
196°–197°			0.7721 (15°)	C_nH_{2n}
216°		0.7745 (20°)		C_nH_{2n}
	216°	0.7684 (20°)		C_nH_{2n+2}
214°–216°			0.7804 (15°)	C_nH_{2n}

Warren found no single body at 162° ; his other hydrocarbons correspond in boiling points with those described in this paper. The series C_nH_{2n} of Warren, with a series of the same numerical composition in Russian oil, led to the suggestion that the naphtenes might form an essential part of Pennsylvania oil. This belief was encouraged by statements that found their way into works on petroleum, that Markownikoff discovered the naphtenes also in Pennsylvania oil. The statement that Markownikoff investigated Pennsylvania petroleum is indeed erroneous,* and a closer study shows that the naphtenes cannot be contained in Pennsylvania petroleum in any considerable quantity on account of their higher specific gravity as already shown (page 143):

Fraction. Unpurified.	Fraction. Purified.	Specific Gravity. Mabery.	Specific Gravity. Markownikoff.	Series.
163°–164°		0.7684		C_nH_{2n}
	163°–164°	0.7479		C_nH_{2n+2}
	160°–162°		0.795 (0°)	C_nH_{2n}
	180°–185°		0.8119 (0°)	C_nH_{2n}
196°–197°		0.7673		C_nH_{2n}
	196°–197°	0.7581		C_nH_{2n+2}
	196°		0.8055 (14°)	C_nH_{2n}
214°–216°		0.7745		C_nH_{2n}
	214°–216°	0.7684		C_nH_{2n+2}

* In a private communication, I am informed by Professor Markownikoff that he has not included Pennsylvania petroleum in his investigations.

Even the mixtures that the crude Pennsylvania distillates have proved to be are much lower in specific gravity than those with the same boiling points from Russian oil. After purification, the Pennsylvania distillates unquestionably have the composition of the series C_nH_{2n+2}.

Allusion has been made to the great difficulty in removing entirely the constituent with less hydrogen from the distillates prepared for analysis, and also to the fact that, even after the most thorough purification, the specific gravity of the purified distillate is appreciably higher than that of the hydrocarbon with the same boiling point prepared by synthetic methods. These facts may indicate the presence in small quantity of naphtenes which are acted on only very slowly by reagents, especially when largely diluted in the main body of the principal constituent.

Structure of the Petroleum Hydrocarbons, 160°–216°.

In comparing the petroleum hydrocarbons with the corresponding bodies synthetically prepared, it is but fair to state that the literature of the latter is not altogether satisfactory. The properties of normal decane as it was prepared by Lachowicz,* by the action of sodium on a mixture of normal octyl bromide and ethyl iodide, and also by Krafft,† by heating caprinic acid with a mixture of hydriodic acid and phosphoric pentachloride, seem to define the corresponding petroleum hydrocarbon as the normal compound.

The boiling point of the hydrocarbon synthetically prepared is 173° under 760 mm., and its specific gravity 0.7456 at 0°. The boiling point assigned by me to petroleum decane is 173°.5, and its specific gravity at 20° is (from Pennsylvania petroleum) 0.7486. Evidently the decane obtained by Thorp and Young by heating solid paraffine, boiling at 166°–168°, specific gravity 0.7394 at 13°.5, is an impure normal hydrocarbon.

A decane has been obtained by several methods, boiling at various temperatures between 157° and 162°. Active diamyl boiling at 159°–162°, specific gravity 0.7463 at 22°, with a high dextro rotatory power, was obtained by Just, on treating active amyl iodide with sodium. But the petroleum decane has not the same form, since it shows no influence on polarized light. The latter has with greater probability the same form as diisoamyl, obtained by Wurtz on heating isoamyl iodide with sodium. The boiling point of this secondary decane is given by Wurtz as 158°, with no mention of barometric tension, and specific gravity as 0.7413.

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* Ann. Chem. Pharm., CCXX. 179.

† Ber. der deutsch. chem. Gesellsch., XV. 1695.

Petroleum decane boils at 163°, and its specific gravity at 20° is 0.7479. In a similar reaction using amyl bromide, Grimshaw * obtained a decane boiling at 168°, under 751 mm. Either the normal bromide must have been used in this reaction giving normal decane, or the boiling point of the product is too high.

Normal hendecane (or undecane) was prepared by Krafft † from the aldehyde rautenol by the same reaction that he used for decane. Its boiling point is given as 194°.5 under 760 mm., and the specific gravity as 0.7411 at 20°. Since the boiling point, 196°–197°, and specific gravity, 0.7581, of petroleum hendecane and the formula of this body, $C_{11}H_{24}$, determined by its molecular weight, correspond so closely to normal hendecane, it has doubtless the same form. As already explained, the higher specific gravity may be due to a small proportion of a naphtene.

The formula $C_{12}H_{26}$, which represents the petroleum hydrocarbon boiling at 214°–216°, is supported by that of normal dodecane which Krafft ‡ obtained by the reduction of laurinic acid. Normal dodecane boils at 214°.5, atmospheric pressure, and its specific gravity at 20° is 0.7511. The specific gravity of petroleum dodecane was found to be 0.7729.

Relation between Specific Gravity and Chemical Composition of Petroleum Distillates.

One interesting result of the examinations described in this paper, and other papers of this series, is the relation between the chemical composition of the individual hydrocarbons and the density of the crude oils from which they were prepared. Pennsylvania petroleum with the lowest specific gravity, 0.80–0.82, is composed below 220° of the hydrocarbons C_nH_{2n+2}. Ohio oil, next higher in the scale of specific gravity, 0.82–0.85, still contains below 220°, as its principal constituents, hydrocarbons of the same series. As the density increases, in the Canadian oil, specific gravity 0.85–0.88, the series C_nH_{2n+2} represents the principal constituents up to and including decane, boiling point 173°, the higher members having the composition C_nH_{2n}. But oils with higher specific gravity, such as a South American petroleum, specific gravity 0.9480, described in another paper of this series, contain only hydrocarbons of the series C_nH_{2n}, and in Caucasus petroleum, specific gravity 0.88, Markownikoff and Oglobine found as the principal constituents the naphtenes, series C_nH_{2n}.

* Ber. der deutsch. chem. Gesellsch., X. 1602.

† Ibid., X. 1697.

‡ *Loc. cit.*, 1698.

Action of Sulphuric Acid on Petroleum Distillates.

Since the beginning of the petroleum industry, the sole method of refining has depended on agitation with sulphuric acid ; yet, notwithstanding the large quantities of material that sulphuric acid removes, as shown by the immense sludge heaps in the vicinity of the refineries, the refiner has not the slightest notion as to what the acid accomplishes beyond his principal object, which is to prepare acceptable products for the market. Neither has any scientific study been made of this problem, at least in American petroleum, so far as revealed by published statements, but that this is an interesting as well as a difficult subject appears from results described in several papers of this series. That ordinary concentrated sulphuric acid has some effect on the density of petroleum distillates is evident from numerous experiments described in this paper. But without independent evidence, it cannot be determined just what constituents are affected by the acid. That some of these constituents, present in small quantity, are unstable and easily acted on by reagents is evident. The refiner must avoid an elevation of temperature during treatment with the acid, otherwise a color appears in the oil that is difficult to remove without redistillation. Evidently an increase in temperature permits of troublesome chemical changes between the acid and the oil, with the formation of products that remain in solution. The skilful refiner is also careful to remove the acid by washing before adding caustic soda to avoid an objectionable color.

In studying the action of sulphuric acid on different distillates from the Russian oil, Markownikoff and Oglobine * attributed the influence of the acid mainly to its action on the unsaturated hydrocarbons and the oxygen compounds. Having separated a series of unsaturated hydrocarbons from Canadian petroleum, (Mabery and Quayle, unpublished results,) and ascertained the presence of the same bodies in Ohio petroleum,† on account of their unstable character and the ease with which they polymerize alone, or more readily when in combination with sulphuric acid, it is evident that one important office of the acid is the removal of these compounds. With reference to the oxygen compounds in American petroleum, they seem to collect for the most part at least in the distillates above 225°. In the composition of their unpurified distillates, Markownikoff and Oglobine found a considerable difference between the total percentages of carbon and hydrogen and 100 per cent, which they assigned to oxygen. In analysis of unpurified distillates described in this paper, the

* Ann. Chim. Phys., (6.), II. 404. † Proc. Amer. Acad., XVII. 218.

total percentages of carbon and hydrogen in most instances have approached 100 per cent to within the limit of the error of analysis, although it is true that these distillates were subjected to close fractional distillation within 1°, while those of Markownikoff and Oglobine were distilled only a few times within limits of 5°. In all the distillations of Pennsylvania, Ohio, and Canadian petroleum, a slight coloration of the still residue after a long series has been observed, which may be due to a small amount of oxygen compounds.

On standing with metallic sodium, all the unpurified distillates described in this paper deposit flocculent precipitates, more or less colored, which are evidently products of decomposition. This cannot be due to the action on the principal hydrocarbon, since when purified such action by sodium is not observed. Neither should the aromatic hydrocarbons behave in this manner toward sodium. These precipitates must be formed from the oxygen or the nitrogen compounds in the oils, probably from the former. They cannot be due to decomposition of sulphur compounds, since Pennsylvania oil contains only a very small percentage of sulphur, and the other distillates were all treated with alcoholic mercuric chloride. It is quite probable that ordinary sulphuric acid combines to a certain extent with some of the aromatic hydrocarbons. A more extended study of the action of sulphuric acid on a larger scale as in refining, would doubtless be interesting and profitable.

Concerning the action of fuming sulphuric acid, no further explanation is necessary than has been given in connection with the experiments which describe its behavior toward these petroleum distillates.

So far as possible, all details of this work have been carried on under my immediate and constant personal supervision. For efficient aid I am indebted to the following gentlemen: Messrs C. A. Soch, private assistant, 1894–95; E. Davidson, private assistant, 1895–96; E. J. Hudson, molecular weight determinations, and other aid mainly in connection with the chlorine derivatives of the hydrocarbons; W. F. Priebe, who selected a portion of the work on the Pennsylvania distillates as the subject of a thesis for the degree of Bachelor of Science; and Messrs Giessen, Watson, Worstall, Piwonka, Shaw, and Walker, for faithful assistance in the routine work of distillation and combustions.

The work now in progress includes a study of the pentanes, hexanes, and heptanes in Pennsylvania petroleum, and the composition of the portions of Pennsylvania, Ohio, Canadian, Berea Grit, and South American petroleums between 216° and 350°.